

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : A61K 7/06, 7/00, 7/50	A1	(11) International Publication Number: WO 00/40213 (43) International Publication Date: 13 July 2000 (13.07.00)
(21) International Application Number: PCT/US99/00018 (22) International Filing Date: 4 January 1999 (04.01.99) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): SAKO, Takashi [JP/JP]; 2-3-202, Uozakikitamachi 6-chome, Higashinada-ku, Kobe 658-0082 (JP). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HAIR CONDITIONING LAYERED GEL COMPOSITION CONTAINING A HIGH MELTING POINT COMPOUND (57) Abstract Disclosed is a hair conditioning composition comprising by weight: (1) at least about 3 % of a high melting point compound having a melting point of at least about 25 °C; (2) an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof; (3) a breakable visible particle comprising structural material selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof; and (4) an aqueous carrier; wherein the composition shows a DSC profile having substantially no peaks larger than about 3mJ/mg from about 40 °C to about 55 °C.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

HAIR CONDITIONING LAYERED GEL COMPOSITION CONTAINING A HIGH MELTING POINT COMPOUND

5

TECHNICAL FIELD

10 The present invention relates to hair conditioning compositions having a layered gel structure comprising a breakable visible particle. The present invention relates to hair conditioning compositions. The present invention further relates to a suitable method of making the hair conditioning compositions hereof.

BACKGROUND

15 Human hair becomes soiled due to its contact with the surrounding environment and from sebum secreted from the scalp. The soiling of the hair causes it to have a dirty or greasy feel, and an unattractive appearance. The soiling of the hair necessitates shampooing with regularity.

Shampooing cleans the hair by removing excess soil and sebum.
20 However, shampooing can leave the hair in a wet, tangled, and generally unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils and other natural conditioning and moisturizing components. The hair can further be left with increased levels of static upon drying which can interfere with combing and
25 result in a condition commonly referred to as "fly-away hair", or contribute to an undesirable phenomena of "split ends", particularly for long hair.

A variety of approaches have been developed to alleviate these after-shampoo problems. These approaches range from post-shampoo application of hair conditioner such as leave-on and rinse-off products, to hair conditioning
30 shampoos which attempt to both cleanse and condition the hair from a single product. Although some consumers prefer the ease and convenience of a shampoo which includes conditioners, a substantial proportion of consumers prefer the more conventional conditioner formulations which are applied to the hair as a separate step from shampooing, usually subsequent to shampooing.
35 Conditioning formulation can be in the form of rinse-off products or leave-on

products, and can be in the form of an emulsion, cream, gel, spray, or mousse. Such consumers who prefer the conventional conditioner formulations value the relatively higher conditioning effect, or convenience of changing the amount of conditioning depending on the condition of hair or portion of hair.

5 Hair conditioning compositions have conventionally been based on the combination of a cationic surfactant, which is generally a quaternary ammonium compound, in combination with various conditioning agents such as polymers, silicone conditioning agents, hydrocarbon and other organic oils, and high melting point compounds such as fatty alcohols. It is known that the combination
10 of a cationic surfactant and a fatty alcohol generally provides a thick, creamy texture which is favorable to some consumers. However, when used at increased levels, fatty alcohols may crystallize and isolate from the matrix of the conditioning composition. Consequently, the increased level of fatty alcohols may not completely contribute toward providing conditioning benefits. Certain
15 phase structures for the combination of quaternary ammonium compounds and fatty alcohol compounds have been suggested in the art such as in Japanese Kokai Patent Publication (A) S61-286311. Yet, these compositions are not capable of delivering satisfactory conditioning benefit both when the hair is wet and also after it has dried.

20 Based on the foregoing, there remains a desire to provide hair conditioning compositions containing an increased level of high melting point compounds wherein the increased level of high melting point compounds can contribute effectively toward providing conditioning benefits. There is also a desire to provide hair conditioning compositions which provide hair conditioning
25 compositions which can provide improved conditioning benefits such as smoothness, softness, and ease of combing, both when the hair is wet and also after it has dried. There is further a desire to provide hair conditioning compositions which provide favorable aesthetic benefits. There is still further a desire to provide such hair conditioning compositions by a convenient method.

30 None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

35 The present invention is directed to a hair conditioning composition comprising by weight:

- (1) at least about 3% of a high melting point compound having a melting point of at least about 25°C;
 - (2) an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof;
 - 5 (3) a breakable visible particle comprising structural material selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof; and
 - (4) an aqueous carrier;
- 10 wherein the composition shows a DSC profile having substantially no peaks larger than about 3mJ/mg from about 40°C to about 55°C.

The present invention is also directed to a suitable method of making the hair conditioning composition.

These and other features, aspects, and advantages of the present
15 invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out
20 and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

25 Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such
30 weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

The aspects and embodiments of the present invention set forth in this document have many advantages. For example, the hair conditioning
35 compositions of the present invention provide improved conditioning benefits

such as smoothness, softness, and ease of combing, both when the hair is wet and also after it has dried. The hair conditioning compositions of the present invention are suitable for product forms to leave on the hair, or rinse off from the hair.

5 LAYERED GEL STRUCTURE

The hair conditioning compositions herein are those which have a layered gel structure, the layered gel structure made by a high melting point compound and a quaternary compound. The existence of a layered gel structure can be detected by differential scanning calorimetry (hereinafter referred to as "DSC") measurement of the composition. A profile chart obtained by DSC measurement describes chemical and physical changes of the scanned sample that involve an enthalpy change or energy gradient when the temperature of the sample is fluctuated. As such, the phase behavior and interaction among components of hair conditioning compositions of the present invention can be understood by their DSC profiles. DSC measurement of compositions of the present invention can be conducted by any suitable instrument available. For example, DSC measurement can be suitably conducted by Seiko DSC 6000 instrument available from Seiko Instruments Inc. In a typical measurement procedure, a sample is prepared by sealing an appropriate amount of the composition into a container made for DSC measurement and sealed. The weight of the sample is recorded. A blank sample i.e; an unsealed sample of the same container is also prepared. The sample and blank sample are placed inside the instrument, and run under a measurement condition of from about -50°C to about 130°C at a heating rate of from about 1°C/minute to about 10°C/minute. The area of the peaks as identified are calculated and divided by the weight of the sample to obtain the enthalpy change represented by unit, mJ/mg.

When the compositions comprising the essential components of the present invention form a layered gel structure, the DSC profile shows substantially no peaks larger than about 3 mJ/mg from about 40°C to about 55°C. The position of the peaks are identified by the peak top position. It is believed that a composition formed predominantly with a layered gel structure shows a relatively stable phase behavior during the temperature range of from about 40°C to about 55°C.

A layered gel structure can be distinguished from spherical crystalline phase structures. By definition, spherical crystalline phase structures include, for

example, phases encompassing solid crystals at random, the M-phase structure as defined in pages 83 to 84 of "Physicochemistry of Cetyl Alcohol" issued by Fragrance Journal Ltd. 1992, and onion-like spherical layers of liquid crystals as taught in Japanese Kokai Patent Publication (A) S61-286311.

5 As taught in the references cited above, spherical crystalline phase structures encompass either crystals or lamellar liquid crystals. Such crystals or lamellar liquid crystals are believed to be made solely by a high melting point compound, or by a combination of a high melting point compound and a quaternary compound. It is believed that the DSC profile of a composition
10 formed predominantly with spherical crystalline phase structures shows alteration of phase, i.e; non-stable phase behaviour due to the crystals and/or liquid crystals during the temperature range of from about 40°C to about 55°C.

The difference of a layered gel structure and spherical crystalline phase structures can also be identified by the cyro scanning electron micrographs
15 (hereinafter referred to as "SEM") of the compositions. A layered gel structure shows flexible layers, the layers being linear, curved, or waved, but not spherical. In contrast, the spherical crystalline phase structures either do not show any systematic patterns, or show onion-like spherical layers.

The hair conditioning compositions of the present invention which have a
20 layered gel structure are believed to provide improved conditioning benefits over the same composition which do not have a layered gel structure. Without being bound by theory, it is believed that the solid crystals and/or liquid crystals of high melting point compounds contained in spherical crystalline phase structures cannot be effectively spread onto and deposited on the surface of the hair.
25 Consequently, the high melting point compounds incorporated in spherical crystalline phase structures contribute less than those incorporated in a layered gel structure with regard to providing conditioning benefit to the hair.

HIGH MELTING POINT COMPOUNDS

The hair conditioning composition of the present invention comprises by
30 weight at least about 3%, preferably from about 3% to about 10%, more preferably from about 4.5% to about 8% of a high melting point compound. The high melting point compound herein has a melting point of at least about 25°C and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof.
35 The high melting point compound, together with the quaternary compound, make

the layered gel structure.

Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of

compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, *i.e.* a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C₁-C₃₀ alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from Shin Nihon Rika (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and chol sterol having tradename NIKKOL AGUASOME LA

available from Nikko.

EMULSIFYING AGENT

The hair conditioning composition of the present invention comprises an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof. The emulsifying agent herein help provide a layered gel structure to the composition. The emulsifying agent is comprised at a level of preferably from about 0.5% to about 5%, more preferably from about 1% to about 3% by weight of the composition.

Amines

Amines are suitable as emulsifying agents. Primary, secondary, and tertiary fatty amines are useful. Particularly useful are tertiary amido amines having an alkyl group of from about 12 to about 22 carbons. Exemplary tertiary amido amines include: stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldiethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and arachidylbehenylamine. Useful amines in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al.

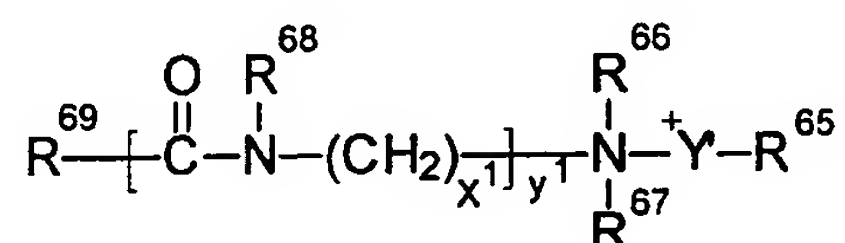
These amines can also be used in combination with acids such as *l*-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, *l*-glutamic hydrochloride, maleic acid, and mixtures thereof; more preferably *l*-glutamic acid, lactic acid, citric acid. The amines herein are preferably partially neutralized with any of the acids at a molar ratio of the amine to the acid of from about 1 : 0.3 to about 1 : 2, more preferably from about 1 : 0.4 to about 1 : 1.

Betaines

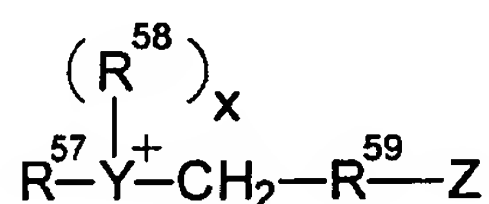
Betaines are suitable as emulsifying agents. Betaines useful herein may

have some surfactant properties, but are generally too low to provide good cleaning properties.

Betaines useful herein are those having the following two formulae:



5 wherein: R^{65} is COO^- or $CH(OH)CH_2SO_3^-$, preferably COO^- ; R^{66} and R^{67} , independently, are hydrogen, alkyl of 1 to about 4 carbons, CH_2COO^- , CH_2CH_2OH , $CH_2CH_2OCH_2CH_2COO^-$, or $(CH_2CH_2O)_xH$ wherein x is an integer from 1 to about 25, preferably methyl or ethyl; R^{68} is hydrogen or alkyl of 1 to about 4 carbons, preferably hydrogen; R^{69} is a straight or branched, saturated or unsaturated alkyl of about 16 to about 30 carbon atoms, preferably a straight saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; Y is an alkyl of 1 to about 4 carbons, preferably methyl; m is an integer from 1 to about 7, preferably from 1 to about 4; n is 1 or 0; and $^-$ is hydrogen or an alkali metal, 10 alkaline earth metal, or ammonium; and



wherein R^{57} is a saturated or unsaturated alkyl, alkenyl, or hydroxy alkyl of from about 16 to about 30 carbon atoms, preferably a saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; Y is nitrogen, phosphorus or sulfur atom; 20 R^{58} is an alkyl or monohydroxyalkyl group containing 1 to about 4 carbon atoms; p is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^{59} is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms; Z is a carboxylate, sulfonate, sulfate, phosphonate, or phosphate; and $^-$ is as previously defined. 25

Examples of betaines useful herein include: alkylbetaines such as cetyldimethylcarboxymethylbetaine, stearyldimethylcarboxymethylbetaine, isostearyldimethylcarboxymethylbetaine, behenyldimethylcarboxymethylbetaine, ol-yldimethylcarboxymethylbetaine, stearyl-bis-(2-hydroxypropyl) 30 carboxymethylbetaine, oleyldimethyl-γ-carboxypropylbetaine, and stearyldihydroxyethylbetaine; amido betaines such as

cetylamidodimethylcarboxymethyl betaine, isostearamidopropyl betaine, isostearylamidodimethylcarboxymethyl betaine, and stearylamidodimethylcarboxypropyl betaine; amidosulfobetaines such as stearylamidodimethylsulfopropylbetaine; sulfobetaines such as 5 stearyldimethylsulfopropylbetaine; sultaines such as stearyldimethylpropylsultaine; and amidosultaines. Commercially available material highly suitable for use herein include stearyl dimethyl betaine with tradename Rikabion A-700 available from Shin Nihon Rika, oleyl dimethyl betaine with tradename Rikabion A-300 available from Shin Nihon Rika, and 10 stearyl dihydroxyethyl betaine with tradename Anon AB 202 available from Nihon Oil & Fats.

Nonionic Compounds

Nonionic compounds are suitable as emulsifying agents. Nonionic compounds useful herein include those compounds produced by condensation 15 of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Although nonionic compounds herein may have some surfactant properties, they are generally too low to provide good cleaning properties.

Preferred nonlimiting examples of nonionic compounds herein include the 20 following:

(1) polyethylene oxide condensates of alkyl phenols, *e.g.*, the condensation products of alkyl phenols having an alkyl group containing from about 16 to about 30 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in 25 amounts equal to from about 2 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

30 (3) condensation products of aliphatic alcohols having from about 16 to about 30 carbon atoms, in either straight chain or branched chain configurations, with ethylene oxide, *e.g.*, a stearyl alcohol ethylene oxide condensate having from about 2 to about 30 moles of ethylene oxide per mole of stearyl alcohol;

(4) long chain tertiary amine oxides of the formula $[R^{70}R^{71}R^{72}N \rightarrow O]$ 35 where R^{70} contains an alkyl, alkenyl or monohydroxy alkyl radical of from about

16 to about 30 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R^{71} and R^{72} contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

5 (5) long chain tertiary phosphine oxides of the formula $[R^{73}R^{74}R^{75}P \rightarrow O]$ where R^{73} contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 16 to about 30 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and R^{74} and R^{75} are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

10 (6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 16 to about 30 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

15 (7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which discloses APS surfactants having a hydrophobic group with about 8 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or
20 unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxyethylene alkyl ethers such as those of the formula
25 $R^{76}O(CH_2CH_2)_{x2}H$ and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula $R^{76}(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_{x2}OH$, wherein $x2$ is from 1 to about 200, preferably from about 20 to about 100, and R^{76} is an alkyl having from about 16 to about 30 carbon atoms.

BREAKABLE VISIBLE PARTICLE

30 The compositions of the present invention comprise a breakable visible particle. By definition, a breakable visible particle is a particle which can be distinctively detected as an individual particle by the naked eye when comprised in the present composition, which is stable in the present composition, yet which is breakable upon use. The breakable visible particle can be of any size, color,
35 or shape, according to the desired characteristic of the product, so long as it is

distinctively detected as an individual particle by the naked eye. Generally, the breakable visible particle has an average diameter of from about 50 μ m to about 3000 μ m, preferably from about 100 μ m to about 1000 μ m, more preferably from about 300 μ m to about 1000 μ m. By stable, it is meant that the breakable visible particles are not disintegrated, agglomerated, or separated under normal shelf conditions. By being breakable, it is meant that the breakable visible particles can be disintegrated with little shear on the hand with the fingers upon use.

The breakable visible particles herein are used at levels which provide the composition with a favorable aesthetic benefit, according to the desired characteristic of the product, typically up to about 10% by weight, preferably from about 0.01% to about 5% by weight of the composition.

The breakable visible particle herein comprises a structural material and preferably an encompassed material.

The structural material provides a certain strength to the breakable visible particle so that they retain their distinctively detectable structure in the present composition under normal shelf conditions, while they can be broken and disintegrated with very little shear on the hand with the fingers upon use. Preferably, the breakable visible particles have a compression strength of about 1 to about 200 grams per particle. Compression strength can be suitably measured with a batch of 20 particles using TA-XT2 Texture Analyzer supplied by Stable Micro Systems Ltd. under the following conditions:

Mode: Measure force in compression
Test speed: 0.1 mm/s
Distance: 0.8 mm
Trigger type: Auto - 10g
Accessory: 25mm cylinder probe (P/25) on acrylate resin plate using 5kg load cell

Further, after the breakable visible particles are disintegrated, they leave little to no residual feeling on the hand, preferably no fragment particles of more than about 10 μ m.

The structural material comprises components selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof. Preferably, components having different water solubility are selected from the above mentioned group to make the structural material. More preferably, the

structural material comprises components selected from the group consisting of cellulose, cellulose derivatives, saccharides, and mixtures thereof. Still preferably, the structural material comprises a mixture of cellulose, cellulose derivatives, and saccharides.

- 5 Exemplary components useful for making the structural material include: polysaccharide and saccharide derivatives such as crystalline cellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate phthalate, cellulose nitrate, ethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, hydroxypropylmethylcellulose phthalate, methyl cellulose, sodium
- 10 carboxymethylcellulose, gum acacia (gum arabic), agar, agarose, maltodextrin, sodium alginate, calcium alginate, dextran, starch, galactose, glucosamine, cyclodextrin, chitin, amylose, amylopectin, glycogen, laminaran, lichenan, curdlan, inulin, levan, pectin, mannan, xylan, alginic acid, arabic acid, glucomannan, agarose, agarpectin, prophyran, carrageenen, fucoidan,
- 15 glycosaminoglycan, hyaluronic acid, chondroitin, peptidoglycan, lipopolysaccharide, guar gum, starch, and starch derivatives; oligosaccharides such as sucrose, lactose, maltose, uronic acid, muramic acid, cellobiose, isomaltose, planteose, melezitose, gentianose, maltotriose, stachyose, glucoside and polyglucoside; monosaccharides such as glucose, fructose, and mannose.
- 20 Components which may further be comprised in the structural material include; synthetic polymers such as acrylic polymers and copolymers including polyacrylamide, poly(alkyl cyanoacrylate), and poly(ethylene-vinyl acetate), and carboxyvinyl polymer, polyamide, poly(methyl vinyl ether-maleic anhydride), poly(adipyl-L-lysine), polycarbonate, polyterephthalamide, polyvinyl acetate
- 25 phthalate, poly(terephthaloyl-L-lysine), polyarylsulfone, poly(methylmethacrylate), poly(ϵ -caprolactone), polyvinylpyrrolidone, polydimethylsiloxane, polyoxyethylene, polyester, polyglycolic acid, polylactic acid, polyglutamic acid, polylysine, polystyrene, poly(styrene-acrylonitrile), polyimide, and poly(vinyl alcohol); and other material such as fat, fatty acid, fatty alcohol, milk solids,
- 30 molasses, gelatin, gluten, albumin, shellac, caseinate, bees wax, carnauba wax, spermaceti wax, hydrogenated tallow, glycerol monopalmitate, glycerol dipalmitate, hydrogenated castor oil, glycerol monostearate, glycerol distearate, glycerol tristearate, 12-hydroxystearyl alcohol, protein, and protein derivatives; and mixtures thereof. Components herein may be described in other sections as
- 35 useful components for the present composition. The components herein,

however, are substantially used to make the structure of the breakable visible particles, and are substantially not dissolved in the bulk of the present composition under normal shelf conditions.

The breakable visible particle herein may encompass, contain, or be filled
5 with an encompassed material. Such encompassed material can be water soluble or water insoluble, and comprise components such as: cationic polymers, vitamins, antioxidants, refreshing agents, proteins and protein derivatives, herbal extracts, pigments, dyes, antimicrobial agents, chelating agents, UV absorbers, optical brighteners, perfumes, humectants which are generally water soluble,
10 additional conditioning agents which are generally water insoluble, and mixtures thereof. In one embodiment, cationic polymers are preferred encompassed material. In such an embodiment, cationic polymers which tend to destabilize the layered gel structure of the composition can be comprised.

CATIONIC POLYMERS

15 Cationic polymers useful as encompassed material herein include those which are water-soluble. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially
20 clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic
25 nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic
30 charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

35 Any anionic counterions can be utilized for the cationic polymers so long

as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have $C_1 - C_7$ alkyl groups, more preferably $C_1 - C_3$ alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula $R^{118}X$ wherein R^{118} is a short chain alkyl, preferably a $C_1 - C_7$ alkyl, more preferably a $C_1 - C_3$ alkyl, and X is a salt forming anion as defined above.

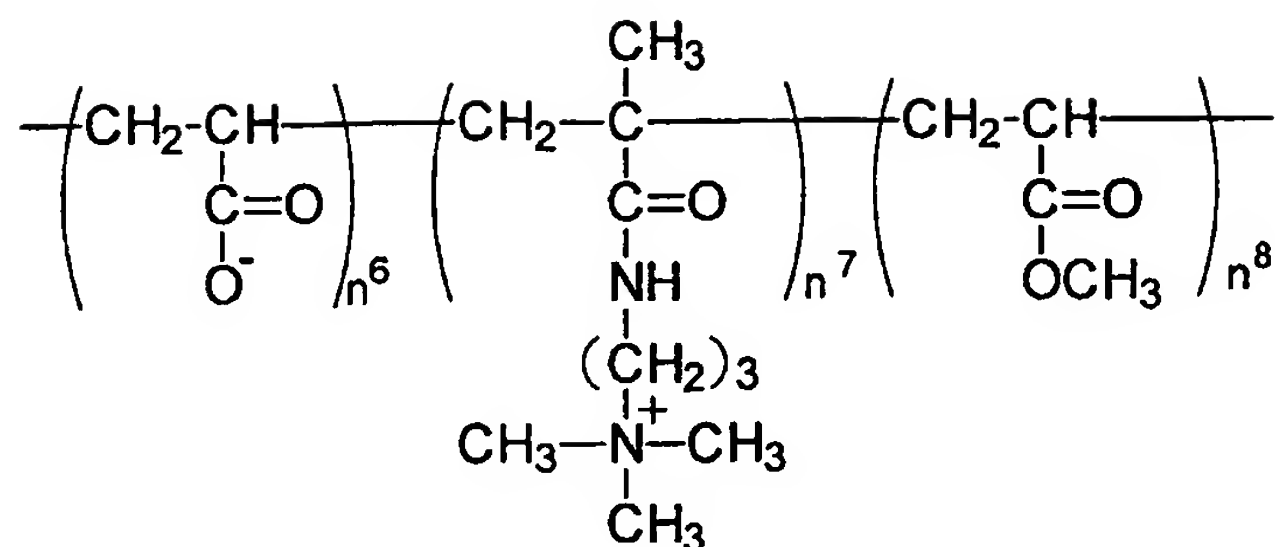
Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt,

trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions
5 of these monomers are preferably lower alkyls such as the C₁ - C₃ alkyls, more preferably C₁ and C₂ alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁ - C₇ hydrocarbyls, more preferably C₁ - C₃, alkyls.

10 The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

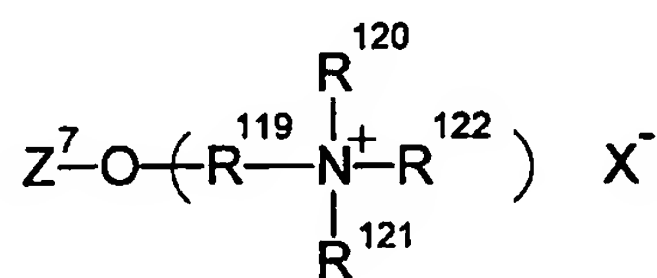
Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g.,
15 chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by
20 CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry
25 (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256.

Other suitable cationic polymers are amphoteric terpolymers consisting of
30 acrylic acid methacrylamidopropyl trimethylammonium chloride and methyl acrylate, having a structure as shown below referred to in the industry (CTFA) as Polyquaternium 47. An example of a suitable commercial material is MERQUAT 2001 wherein the ratio of n⁶:n⁷:n⁸ is 45:45:10 supplied by Calgon Corp.



Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include
 5 those of the formula:



wherein: Z⁷ is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R¹¹⁹ is an alkylene oxyalkylene, polyoxyalkylene, or
 10 hydroxyalkylene group, or combination thereof, R¹²⁰, R¹²¹, and R¹²² independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (*i.e.*, the sum of carbon atoms in R¹²⁰, R¹²¹ and R¹²²) preferably being about 20 or less, and X is as previously described.

15 Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR and LR series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with
 20 lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride commercially
 25 available from Celanese Corp. in their Jaguar R series. Other materials include quaternary nitrogen-containing cellulose ethers (as described in U.S. Patent

3,962,418, and copolymers of etherified cellulose and starch (as described in U.S. Patent 3,958,581.

Particularly useful cationic polymers herein include Polyquaternium-7, Polyquaternium-10, Polyquaternium-24, Polyquaternium-39, Polyquaternium-47, and mixtures thereof.

VITAMINS AND AMINO ACIDS

Vitamins and amino acids useful as encompassed material herein include: water soluble vitamins such as vitamin B1, B2, B6, B12, C, pantothenic acid, pantothenyl ethyl ether, panthenol, biotin, and their derivatives, water soluble amino acids such as asparagine, alanin, indole, glutamic acid and their salts, water insoluble vitamins such as vitamin A, D, E, and their derivatives, water insoluble amino acids such as tyrosine, tryptamine, and their salts.

ANTIOXIDANTS

Antioxidants useful as encompassed material herein include: sesamol, sesamol, gossypol, BHA (butyl hydroxy anisole, BHT (dibutyl hydroxy toluene), nordihydroguaiaretic acid, propyl gallate, phytic acid, and guajacum resin. Synergists for these antioxidants may be included; such as citric acid, ascorbic acid, and malic acid.

REFRESHING AGENTS

Refreshing agents useful as encompassed material herein include menthol and camphor in their d- and dl- forms.

PIGMENTS

Pigments useful as encompassed material herein include inorganic, nitroso, monoazo, disazo, carotenoid, triphenyl methan, triaryl methane, xanthene, quinoline, oxazine, azine, anthraquinone, indigoid, thionindigoid, quinacridone, phthalocianine, botanical, natural colors, including: water soluble components such as those having C. I. Names: Acid Red 18, 26, 27, 33, 51, 52, 87, 88, 92, 94, 95, Acid Yellow 1, 3, 11, 23, 36, 40, 73, Food Yellow 3, Food Green 3, Food blue 2, Food Red 1, 6, Acid Blue 5, 9, 74, Pigment Red 57-1, 53(Na), Basic Violet 10, Solvent Red 49, Acid orange 7, 20, 24, Acid Green 1, 3, 5, 25, Solvent Green 7, Acid Violet 9, 43; water insoluble components such as those having C. I. Names: Pigment Red 53(Ba), 49(Na), 49(Ca), 49(Ba), 49(Sr), 57, Solvent Red 23, 24, 43, 48, 72, 73, Solvent Orange 2, 7, Pigment Red 4, 24, 48, 63(Ca)3, 64, Vat Red 1, Vat blue 1, 6, Pigment Orange 1, 5, 13, Solvent Yellow 5, 6, 33, Pigment Yellow 1, 12, Solvent Green 3, Solvent Violet 13,

Solvent Blue 63, Pigment Blue 15, titanium dioxides, chlorophyllin copper complex, ultramarines, aluminum powder, bentonite, calcium carbonate, barium sulfate, bismuthine, calcium sulfate, carbon black, bone black, chromic acid, cobalt blue, gold, ferric oxides, hydrated ferric oxide, ferric ferrocyanide, magnesium carbonate, manganous phosphate, silver, and zinc oxides.

ANTIMICROBIAL AGENTS

Antimicrobial agents useful as encompassed material include those useful as cosmetic biocides and antidandruff agents anti-itchiness agents including: water soluble components such as piroctone olamine, water insoluble components such as 3,4,4'- trichlorocarbanilide (trichlosan), triclocarban, zinc pyrithione, selenium disulfide, alkylisoquinolinium bromide, biphenamine, thianthol, cantharides tincture, ginger tincture, and capsicum tincture.

CHELATING AGENTS

Chelating agents useful as encompassed material include: 2,2'-dipyridylamine; 1,10-phenanthroline {o-phenanthroline}; di-2-pyridyl ketone; 2,3-bis(2-pyridyl) pyrazine; 2,3-bis(2-pyridyl)-5,6-dihydropyrazine; 1,1'-carbonyldiimidazole; 2,4-bis(5,6-diphenyl-1,2,4-triazine-3-yl)pyridine; 2,4,6-tri(2-pyridyl)-1,3,5-triazine; 4,4'-dimethyl-2,2'dipyridyl; 2,2'-biquinoline; di-2-pyridyl glyoxal {2,2'-pyridil}; 2-(2-pyridyl)benzimidazole; 2,2'-bipyrazine; 3-(2-pyridyl)5,6-diphenyl-1,2,4-triazine; 3-(4-phenyl-2-pyridyl)-5-phenyl-1,2,4-triazine; 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine; 2,3,5,6-tetrakis-(2'-pyridyl)-pyrazine; 2,6-pyridinedicarboxylic acid; 2,4,5-trihydroxypyrimidine; phenyl 2-pyridyl ketoxime; 3-amino-5,6-dimethyl-1,2,4-triazine; 6-hydroxy-2-phenyl-3(2H)-pyridazinone; 2,4-pteridinediol {lumazine}; 2,2'-dipyridyl; and 2,3-dihydroxypyridine.

UV ABSORBER

UV absorbers useful as encompassed material herein can be water soluble or water insoluble, including: p-aminobenzoic acid, its salts and its derivatives (ethyl, isobutyl, glyceryl esters; p-dimethylaminobenzoic acid); anhranilates (i.e., o-aminobenzoates; methyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpinyl, and cyclohexenyl esters); salicylates (amyl, phenyl, benzyl, menthyl, glyceryl, and dipropyleneglycol esters); cinnamic acid derivatives (menthyl and benzyl esters, -phenyl cinnamionitrile; butyl cinnamoyl pyruvate; trihydroxycinnamic acid derivatives (esculetin, methylesculetin, daphn tin, and the glucosides, esculin and daphnin); dibenzalacetone and benzalacetophenone; naphtholsulfonates (sodium salts of 2-naphthol-3,6-

disulfonic and of 2-naphthol-6,8-disulfonic acids); dihydroxy-naphthoic acid and its salts; o-and p-Hydroxybiphenyldisulfonates; quinine salts (bisulfate, sulfate, chloride, oleate, and tannate); quinoline derivatives (8-hydroxyquinoline salts, 2-phenylquinoline); hydroxy- or methoxy-substituted benzophenones; uric and vilouric acids; tannic acid and its derivatives (e.g., hexaethylether); (butyl carbityl) (6-propyl piperonyl) ether; hydroquinone; benzophenones (oxybenzene, sulisobenzene, dioxybenzene, benzoescorcinol, 2,2',4,4'-Tetrahydroxybenzophenone, 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone, octabenzene); 4-Isopropylidibenzoylmethane; butylmethoxydibenzoylmethane; etocrylene; and 4-isopropyl-di-benzoylmethane. Of these, 2-ethylhexyl p-methoxycinnamate, 4,4'-t-butyl methoxydibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyldimethyl p-aminobenzoic acid, digalloyltriolate, 2,2-dihydroxy-4-methoxybenzophenone ethyl 4-[bis(hydroxypropyl)]aminobenzoate, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, 2-ethylhexylsalicylate, glyceryl p-aminobenzoate, 3,3,5-trimethylcyclohexylsalicylate, methylanthranilate, p-dimethyl-aminobenzoic acid or aminobenzoate, 2-ethylhexyl p-dimethylamino-benzoate, 2-phenylbenzimidazole-5-sulfonic acid, 2-(p-dimethylaminophenyl)-5-sulfonicbenzoxazoic acid and mixtures thereof. Preferred sunscreens useful in the compositions of the present invention are 2-ethylhexyl p-methoxycinnamate, butylmethoxydibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyldimethyl p-aminobenzoic acid and mixtures thereof.

OPTICAL BRIGHTENER

Optical brighteners useful as encompassed material herein include compounds which absorb ultraviolet light and re-emit the energy in the form of visible light. Specifically, the optical brighteners useful herein have an absorption, preferably a major absorption peak, between a wavelength of about 1nm and about 420nm, and an emission, preferably a major emission peak, between a wavelength of about 360nm and about 830nm; wherein the major absorption peak has a shorter wavelength than the major emission peak. More preferably, the optical brighteners useful herein have a major absorption peak between a wavelength of about 200nm and about 420nm, and a major emission peak between a wavelength of about 400nm and about 780nm. Optical brighteners may or may not have minor absorption peaks in the visible range between a wavelength of about 360nm and about 830nm. Optical brighteners can be described by other

names in the art and in other industries, such as fluorescent whitening agents, fluorescent brighteners, and fluorescent dyes.

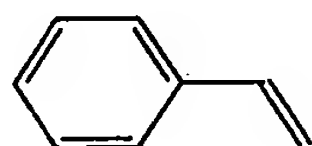
When applied to hair via suitable vehicles, optical brighteners herein provide benefits to the hair in three areas. First, optical brighteners herein alter the color of the hair by emitting light in the visible range. Second, optical brighteners herein enhance the shine of the hair by emitting light in the visible range. Third, optical brighteners herein protect the hair from ultraviolet light by absorbing ultraviolet light.

Optical brighteners in general are based on the structures of aromatic and heteroaromatic systems which provide these unique characteristics. The optical brighteners useful in the present invention can be water soluble and water insoluble, and can be classified according to their base structures, as described hereafter. Preferable optical brighteners herein include polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles.

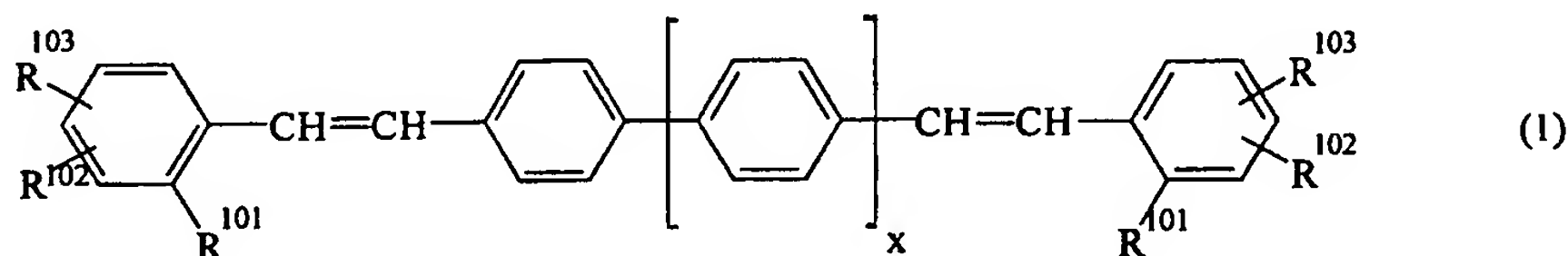
The optical brighteners useful herein are preferably used at levels by weight of the composition of from about 0.001% to about 10%.

Polystyrylstilbenes

Polystyrylstilbenes are a class of compounds having two or more of the following base structure:

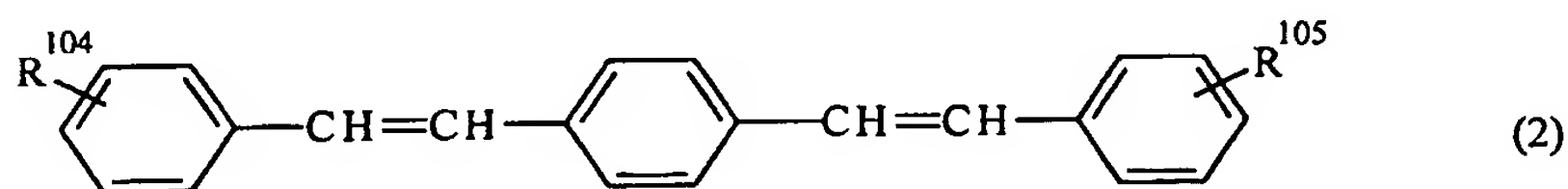


Polystyrylstilbenes useful in the present invention include those having formulae (1), (2) and (3):

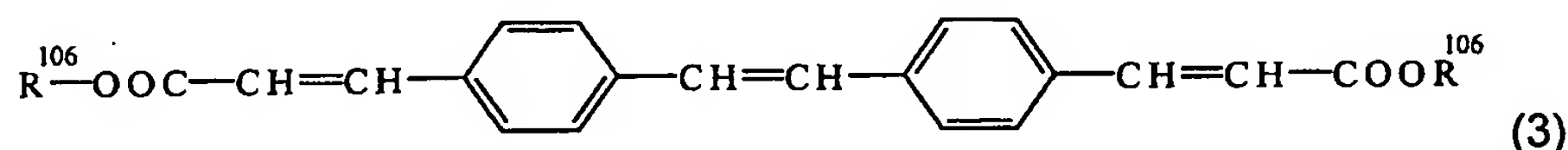


wherein R^{101} is H, OH, SO_3M , $COOM$, OSO_3M , $OPO(OH)OM$, wherein M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- C_1 - C_{30} -alkylammonium, mono-, di- or tri- C_1 - C_{30} -hydroxyalkylammonium or ammonium that is di- or tri-

substituted with by a mixture of C₁-C₃₀-alkyl and C₁-C₃₀-hydroxyalkyl groups;
 or SO₂N(C₁-C₃₀-alkyl)₂, O-(C₁-C₃₀-alkyl), CN, Cl, COO(C₁-C₃₀-alkyl),
 CON(C₁-C₃₀-alkyl)₂ or O(CH₂)₃N⁺(CH₃)₂X⁻ wherein X⁻ is an anion of a
 chloride, bromide, iodide, formate, acetate, propionate, glycolate, lactate,
 5 acrylate, methanephosphonate, phosphite, dimethyl or diethyl phosphite anion;
 CN, or alkyl of 1 to 30 carbons, R¹⁰² and R¹⁰³, independently, are H, SO₃M
 wherein M is as previously defined; and x is 0 or 1; wherein the compound has a
 trans-coplanar orientation or cis-coplanar orientation; preferably x is 1, R¹⁰¹ is
 SO₃Na and R¹⁰² and R¹⁰³ are H; wherein the compound has a trans-coplanar
 10 orientation;



wherein R¹⁰⁴ and R¹⁰⁵, independently, are CN, COO(C₁-C₃₀-alkyl), CONHC₁-
 15 C₄-alkyl, or CON(C₁-C₄-alkyl)₂, wherein the compound has a trans-coplanar
 orientation or cis-coplanar orientation; preferably R¹⁰⁴ and R¹⁰⁵ is 2-cyano,
 wherein the compound has a trans-coplanar orientation; and



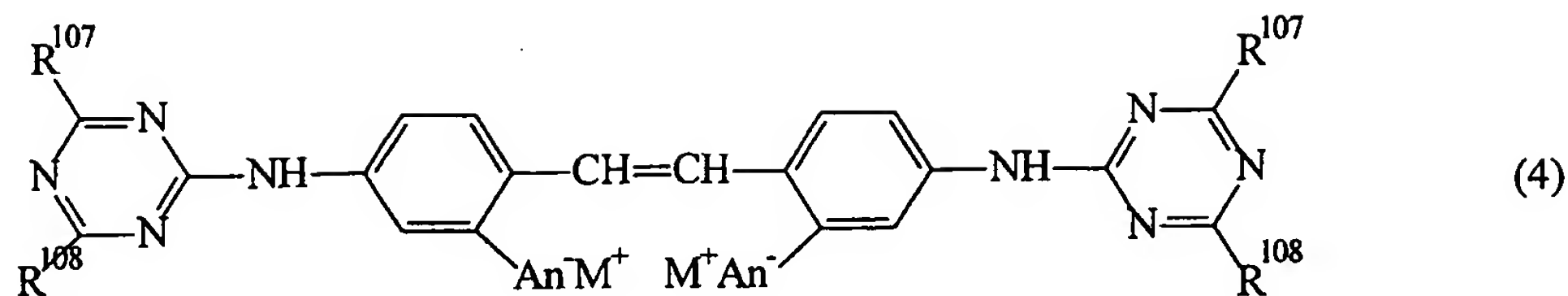
20 wherein each R¹⁰⁶, independently, is H, or alkyl of 1 to 30 carbons; and wherein
 the compound has a trans-coplanar orientation or cis-coplanar orientation,
 preferably a trans-coplanar orientation.

Suitable polystyrylstilbenes include disodium-1, 4'-bis(2-sulfostryl)
 25 bisphenyl (C.I. Fluorescent Brightener 351) with tradename Tinopal CBS-X
 available from Ciba Specialty Chemicals, 1,4-bis(2-cyanostyryl)benzene (C.I.
 Fluorescent Brightener 199) with tradename Ultraphor RN available from BASF.

Triazinstilbenes

Triazinstilbenes are a class of compounds having both triazin and stilbene
 30 structures in the same molecule.

Triazinstilbenes useful in the present invention include those having
 formulae (4):

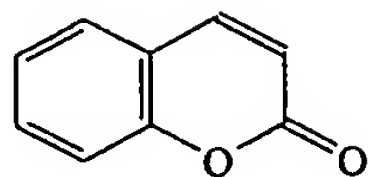


wherein R¹⁰⁷ and R¹⁰⁸, independently, are phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH₂CH₂OH)₂, N(CH₃)(CH₂CH₂OH), NH₂, N(C₁-C₄-alkyl)₂, OCH₃, Cl, NH-(CH₂)₁₋₄SO₃H or NH-(CH₂)₁₋₄OH; An⁻ is an anion of a carboxylate, sulfate, sulfonate, or phosphate, and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R¹⁰⁷ is 2, 5-disulfophenylamino and each R¹⁰⁸ is morpholino; or each R¹⁰⁷ is 2, 5-disulfophenylamino and each R¹⁰⁸ is N(C₂H₅)₂; or each R¹⁰⁷ is 3-sulfophenyl and each R¹⁰⁸ is NH(CH₂CH₂OH) or N(CH₂CH₂OH)₂; or each R¹⁰⁷ is 4-sulfophenyl and each R¹⁰⁸ is N(CH₂CH₂OH)₂; and in each case, the sulfo group is SO₃M in which M is sodium; wherein the compound has a trans-coplanar orientation.

Suitable triazinstilbenes include 4,4'-bis-[(4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid with tradename Tinopal UNPA-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-morpholine-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal AMS-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-(2-hydroxyethyl)methyl amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal 5BM-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4,6-dianilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-ethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, and 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid.

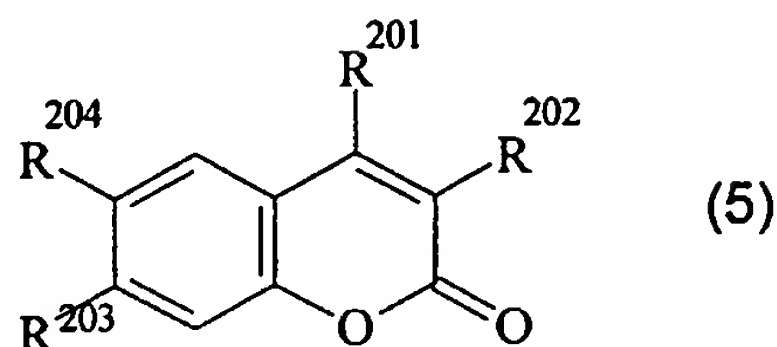
Hydroxycoumarins

Hydroxycoumarins are a class of compounds having the following base coumarin structure and having at least one hydroxy moiety:

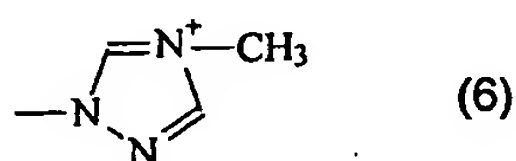


Hydroxycoumarins useful in the present invention include those having formulae (5):

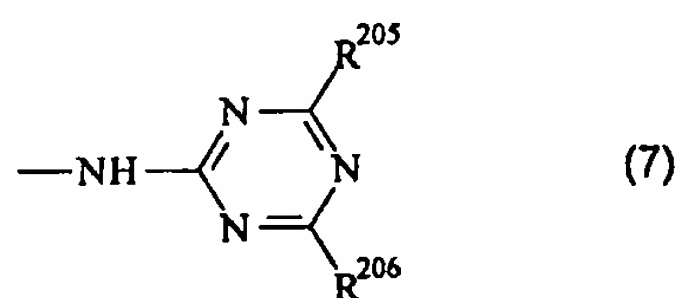
5



wherein R²⁰¹ is H, OH, Cl, CH₃, CH₂COOH, CH₂SO₃H, CH₂OSO₃H, or CH₂OPO(OH)OH, R²⁰² is H, phenyl, COO-C₁-C₃₀-alkyl, glucose, or a group of
10 formula (6):



and R²⁰³ is OH, or O-C₁-C₃₀-alkyl, and R²⁰⁴ is OH or O-C₁-C₃₀ alkyl,
15 glycoside, or a group of the following formula (7):



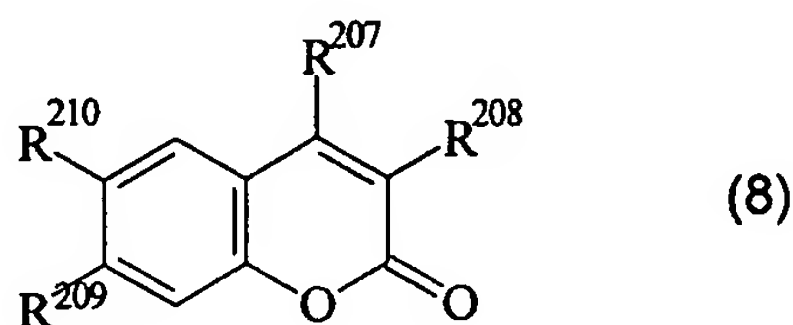
wherein R²⁰⁵ and R²⁰⁶ are independently, phenylamino, mono- or disulfonated
20 phenylamino, morpholino, N(CH₂CH₂OH)₂, N(CH₃)(CH₂CH₂OH), NH₂, N(C₁-C₃₀-alkyl)₂, OCH₃, Cl, NH-(CH₂)₁₋₄SO₃H or NH-(CH₂)₁₋₄OH.

Suitable hydroxycoumarins include 6,7-dihydroxycoumarin available from Wako Chemicals, 4-methyl-7-hydroxycoumarin available from Wako Chemicals, 4-methyl-6,7-dihydroxycoumarin available from Wako Chemicals, esculin
25 available from Wako Chemicals, and umbelliferone (4-hydroxycoumarin) available from Wako Chemicals.

Aminocoumarins

Aminocoumarins are a class of compounds having the base coumarin structure and having at least one amino moiety.

Aminocoumarins useful in the present inventions include those having
5 formulae (8):

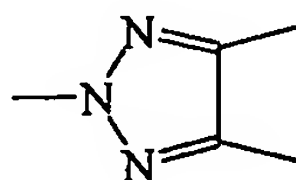


wherein R^{207} is H, Cl, CH_3 , CH_2COOH , CH_2SO_3H , CH_2OSO_3H , or
10 $CH_2OPO(OH)OH$, R^{208} is H, phenyl, or $COOC_1-C_{30}$ alkyl, and R^{209} and R^{210}
are independently H, NH_2 , $N(C_1-C_{30}alkyl)_2$, $NHC_1-C_{30}alkyl$, or $NHCOC_1-$
 $C_{30}alkyl$.

Suitable aminocoumarins include 4-methyl-7,7'-diethylamino coumarin
with tradename Calcofluor-RWP available from BASF, 4-methyl-7,7'-
15 dimethylamino coumarin with tradename Calcofluor-LD available from BASF.

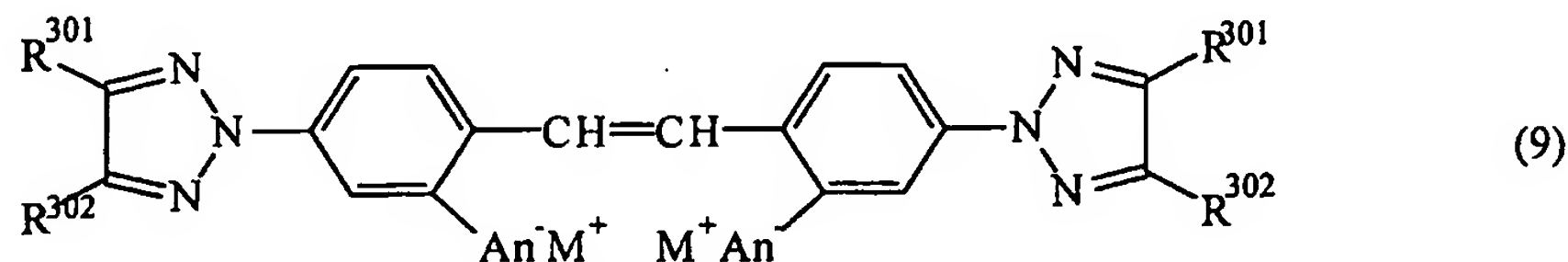
Triazoles

Triazoles are a class of compounds having the following base structure:



20

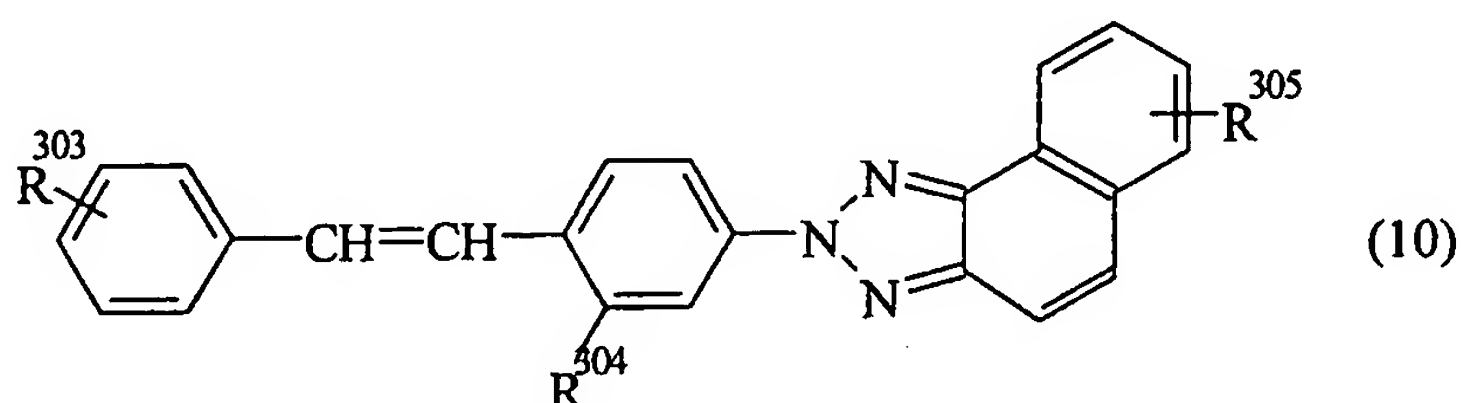
Triazoles useful in the present inventions include those having formulae
(9) through (12) and (15) through (20):



25

wherein R^{301} and R^{302} , independently, are H, $C_1-C_{30}alkyl$, phenyl or
monosulfonated phenyl; An^- and M are as previously defined, wherein the

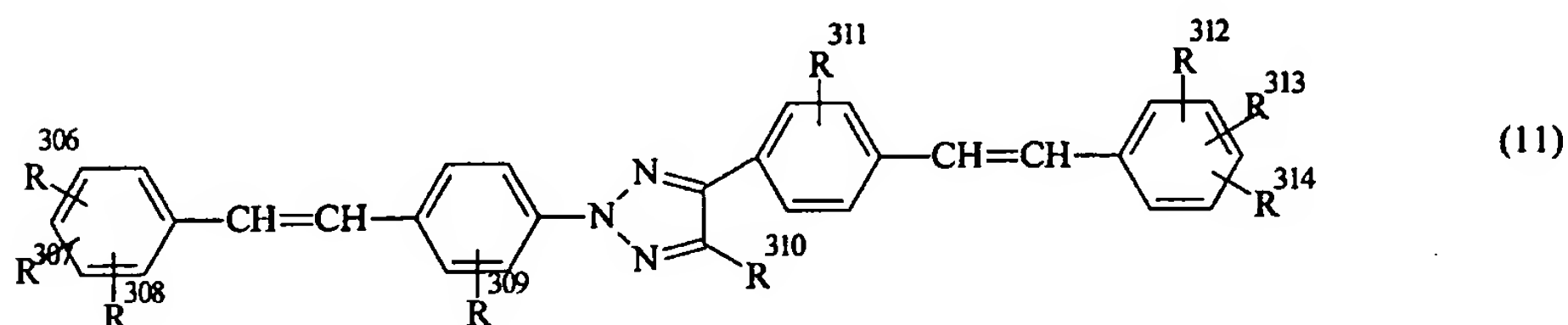
compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R³⁰¹ is phenyl, R³⁰² is H and M is sodium; wherein the compound has a trans-coplanar orientation;



5

wherein R³⁰³ is H or Cl; R³⁰⁴ is SO₃M, SO₂N(C₁-C₃₀-alkyl)₂, SO₂O-phenyl or CN; R³⁰⁵ is H, SO₃M, COOM, OSO₃M, or OPO(OH)OM; and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R³⁰³ and R³⁰⁵ are H and R³⁰⁴ is SO₃M in which M is Na; wherein the compound has a trans-coplanar orientation;

10



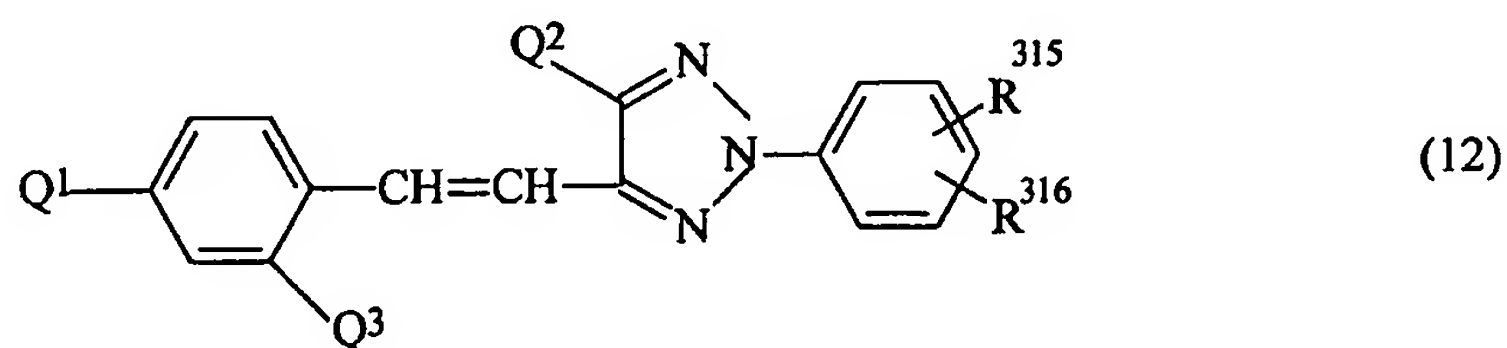
wherein each of R³⁰⁶ and R³¹² independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkylsulfonyl, arylsulfonyl, alkyl, alkoxy, aralkyl, aryl, aryloxy, aralkoxy or cycloalkyl radical, an unsubstituted or substituted 5-membered heterocyclic ring containing 2 to 3 nitrogen atoms or one oxygen atom and 1 or 2 nitrogen atoms, or together with R³⁰⁷ and R³¹³ they represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R³⁰⁷ and R³¹³ independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkyl or alkoxy radical, or together with R³⁰⁶ and R³¹² represent a methylenedioxy, ethylenedioxy,

15

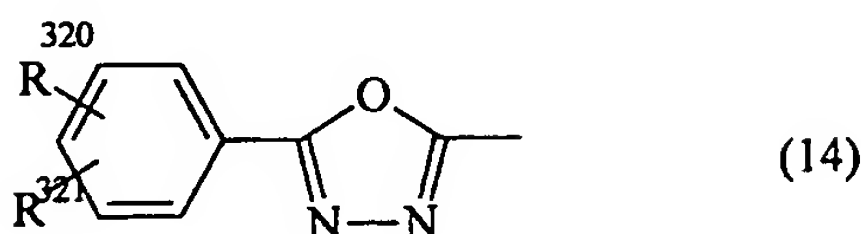
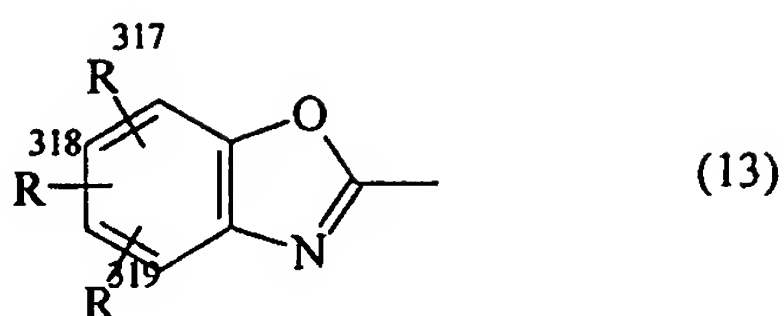
20

25

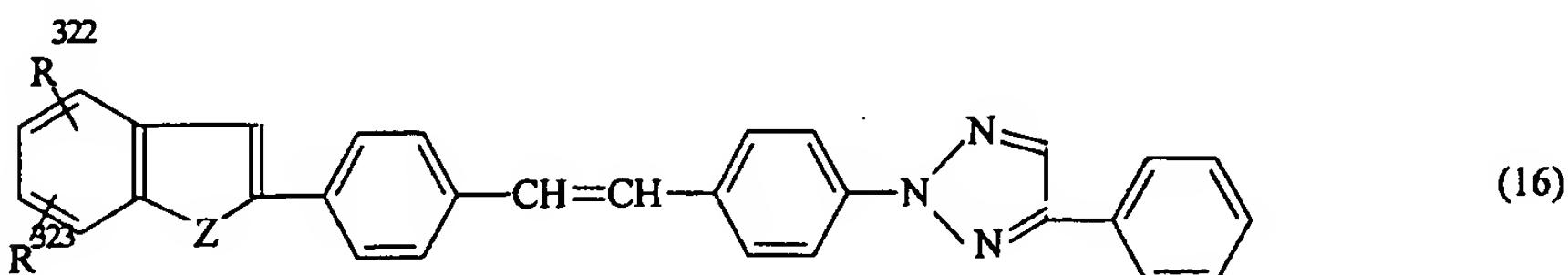
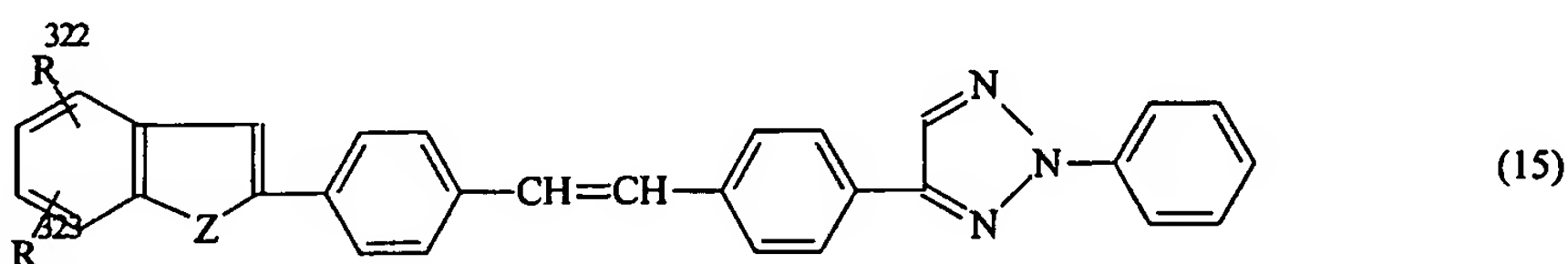
methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R³⁰⁸ and R³¹⁴ independently represents H, a halogen atom or an unsubstituted or substituted alkyl radical, each of R³⁰⁹ and R³¹¹ independently represents H, a halogen atom, a cyano group a sulonic acid group or the salts, esters or amides thereof, or a carboxylic acid group or the salts, esters or amides thereof, and R³¹⁰ independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, alkyl radicals preferably by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, sulfonic acid groups, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; alkoxy radicals can be substituted by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; phenyl, phenylalkyl or phenoxy radicals can be substituted by halogen, cyano, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, sulfo, or alkyl or alkoxy each of 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; possible cycloalkyl radicals are preferably cyclohexyl and cyclopentyl radicals which can be substituted by alkyl of 1 to 30 carbon atoms; possible 5-membered heterocyclic rings are v-triazole, oxazole or 1, 3, 4- oxdiazole radicals which can contain as substituents alkyl radicals of 1 to 4 carbon atoms, halogen, phenyl, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, cyano, benzyl, alkoxy of 1 to 30 carbon atoms, phenoxy or sulfo, whilst two adjacent substituents of the triazole and oxazole radicals together are able to form a substituted or unsubstituted fused benzene nucleus; wherein the compound has a trans-coplanar orientation;



wherein Q¹ denotes one of the ring systems (13) or (14);

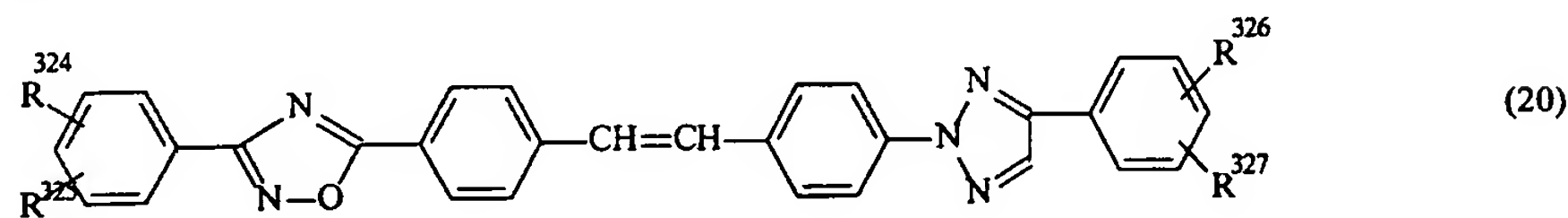
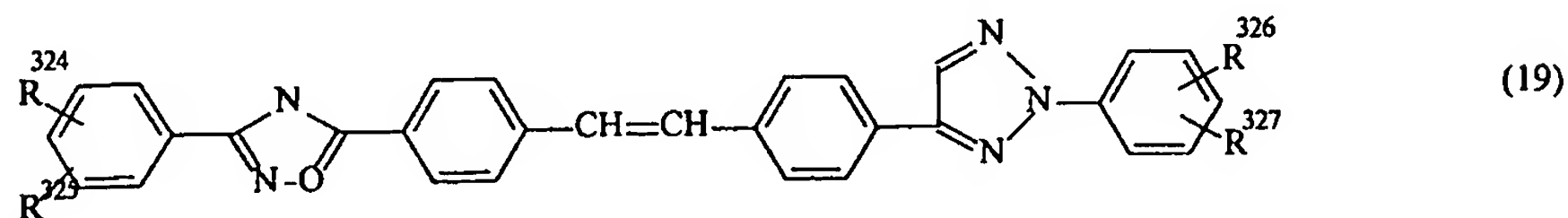
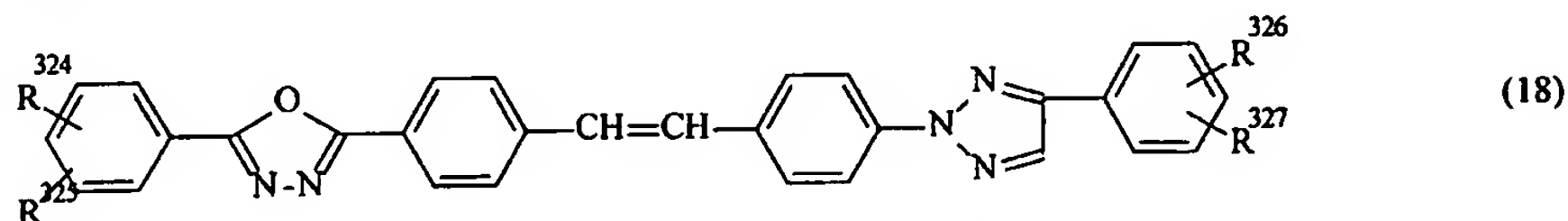
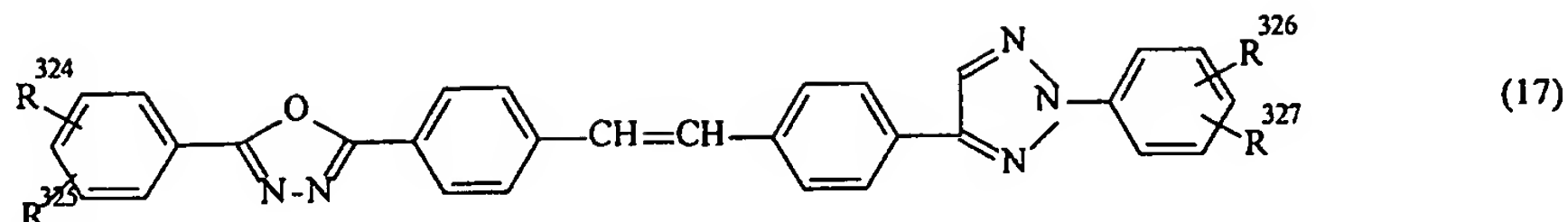


and wherein R³¹⁷ denotes H, alkyl with 1 to 30 carbon atoms, cyclohexyl,
 5 phenylalkyl with C₁-C₃₀ carbon atoms in the alkyl part, phenyl, alkoxy with 1 to
 30 carbon atoms, or Cl, or, conjointly with R³¹⁸, denotes alkylene with 3 to 30
 carbon atoms, R³¹⁸ denotes H or alkyl with 1 to 30 carbon atoms or, conjointly
 with R³¹⁷, denotes alkylene with 3 to 30 carbon atoms, R³¹⁹ denotes H or
 methyl, R³²⁰ denotes H, alkyl with 1 to 30 carbon atoms, phenyl, alkoxy with 1 to
 10 30 carbon atoms, or Cl, or, conjointly with R³²¹, denotes a fused benzene ring,
 R³²¹ denotes H or Cl or conjointly with R³²⁰, denotes a fused benzene ring,
 R³¹⁵ denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon
 atoms or Cl, R³¹⁶ denotes H or Cl, Q² denotes H, Cl alkyl with 1 to 30 carbon
 atoms or phenyl and Q³ denotes H or Cl; wherein the compound has a trans-
 15 coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar
 orientation;



20

wherein R³²² denotes H, Cl, methyl, phenyl, benzyl, cyclohexyl or methoxy,
 R³²³ denotes H or methyl and Z denotes O or S; wherein the compound has a
 trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar
 orientation; and

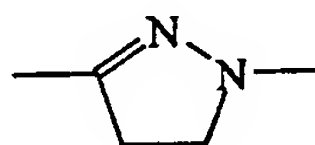


wherein R³²⁴ denotes H, Cl, alkyl with 1 to 30 carbon atoms, phenylalkyl with 1 to 30 carbon atoms, phenyl or alkoxy with 1 to 30 carbon atoms, or R³²⁴ jointly with R³²⁵ denotes a fused benzene radical, R³²⁵ denotes H or methyl or R³²⁵ jointly with R³²⁴ denotes a fused benzene radical, R³²⁶ denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms or alkylsulfonyl with 1 to 30 carbon atoms and R³²⁷ denotes H, Cl, methyl or methoxy; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

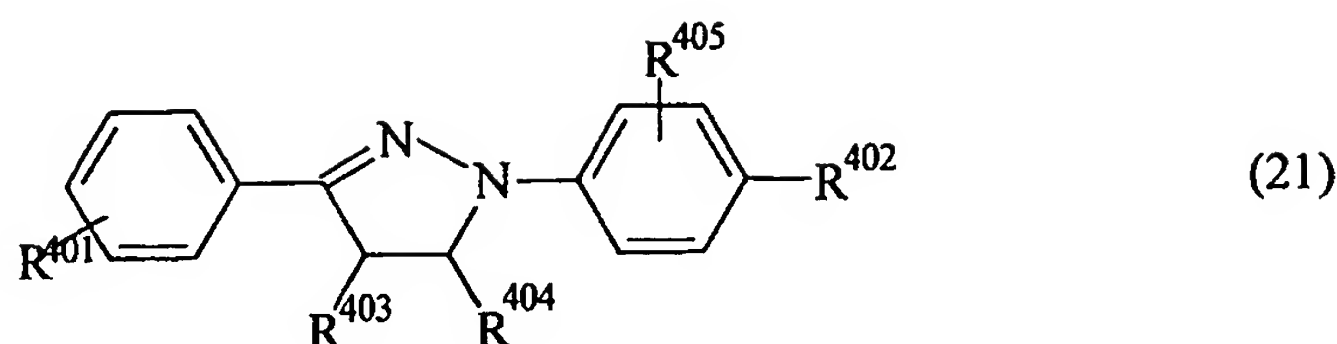
Suitable triazoles include 2-(4-styryl-3-sulfophenyl)-2H-naptho[1,2-d] triazole (C.I. Fluorescent Brightener 46) with tradename Tinopal RBS available from Ciba Specialty Chemicals.

Pyrazolines

Pyrazolines are a class of compounds having the following base structure:

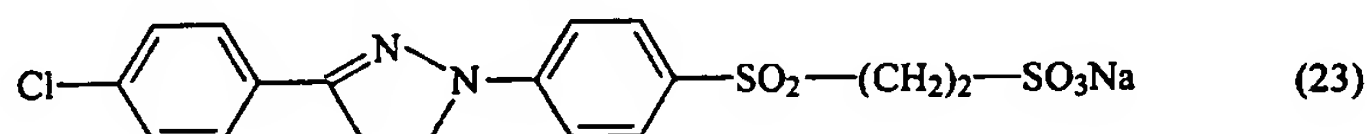
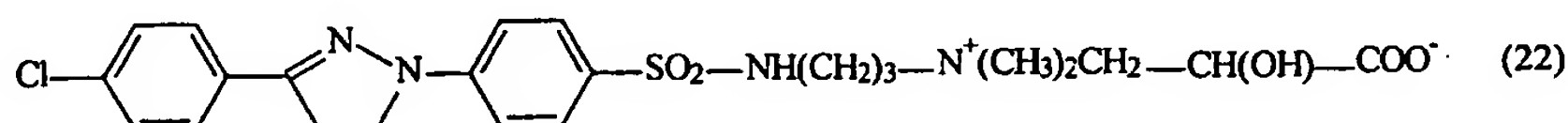


Pyrazolines useful in the present invention include those having formulae (21) through (23):



wherein R⁴⁰¹ is H, Cl or N(C₁-C₃₀-alkyl)₂, R⁴⁰² is H, Cl, SO₃M, SO₂NH₂, SO₂NH-(C₁-C₃₀alkyl), COO-C₁-C₃₀alkyl, SO₂-C₁-C₃₀alkyl, SO₂NH(CH₂)₁₋₄N⁺(CH₃)₃ or SO₂(CH₂)₁₋₄N⁺H(C₁-C₃₀-alkyl)₂An⁻, R⁴⁰³ and R⁴⁰⁴ are the same or different and each is H, C₁-C₃₀alkyl or phenyl and R⁴⁰⁵ is H or Cl; and An⁻ and M are as previously defined, preferably R⁴⁰¹ is Cl, R⁴⁰² is SO₂CH₂CH₂N⁺H(C₁-C₄-alkyl)₂An⁻ in which An⁻ is phosphite and R⁴⁰³, R⁴⁰⁴ and R⁴⁰⁵ are each H; and formulae (22) and (23) shown below.

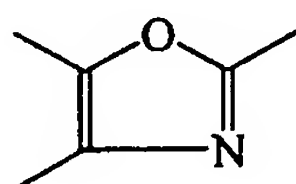
10



Suitable pyrazolines include 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline (C.I. Fluorescent Brightener 121) with tradename Blankophor DCB available from Bayer, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-pyrazoline, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methylphenyl)-2-pyrazoline, 1-<4-{N-[3-(N,N,N-trimethylammonio)propyl]-amidosulfonyl}phenyl>-3-(4-chlorophenyl)-2-pyrazoline methylsulfate, and 1-<4-{2-[1-methyl-2-(N,N-dimethylamino)ethoxy]ethylsulfonyl}phenyl>-3-(4-chlorophenyl)-2-pyrazoline methylsulfate.

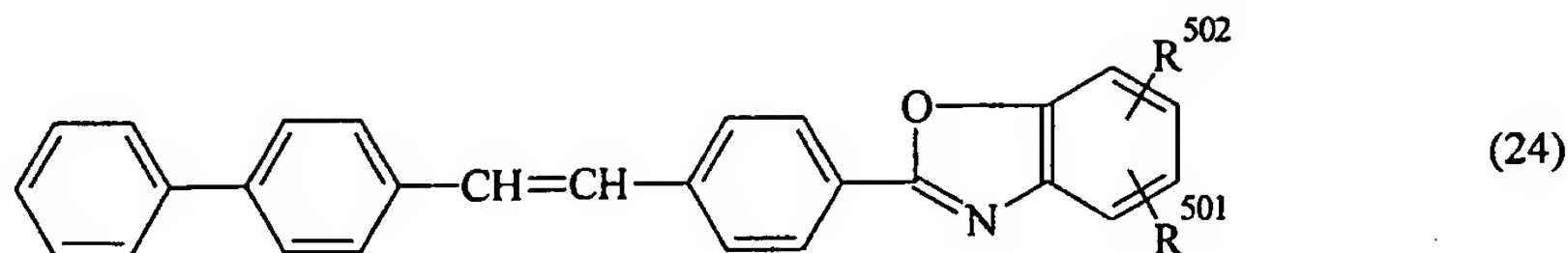
Oxazoles

Oxazoles are a class of compounds having the following base structure:

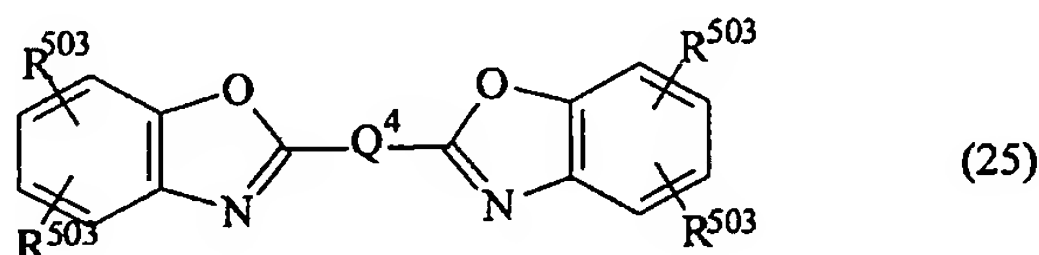


25

Oxazoles useful in the present inventions include those having formulae (24), (25), (26) and (27):

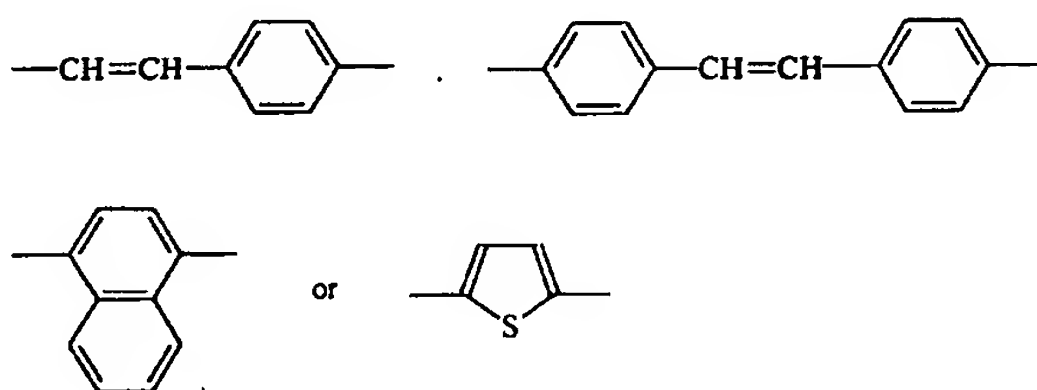


wherein R⁵⁰¹ and R⁵⁰², independently, are H, Cl, C₁-C₃₀alkyl or SO₂-C₁-C₃₀-
 5 alkyl, wherein the compound has a trans-coplanar orientation or cis-coplanar
 orientation; preferably R⁵⁰¹ is 4-CH₃ and R⁵⁰² is 2-CH₃ wherein the compound
 has a trans-coplanar orientation;



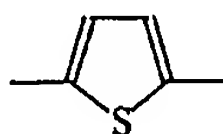
10

wherein R⁵⁰³, independently, is H, C(CH₃)₃, C(CH₃)₂-phenyl, C₁-C₃₀alkyl or
 COO-C₁-C₃₀alkyl, preferably H and Q⁴ is -CH=CH-;

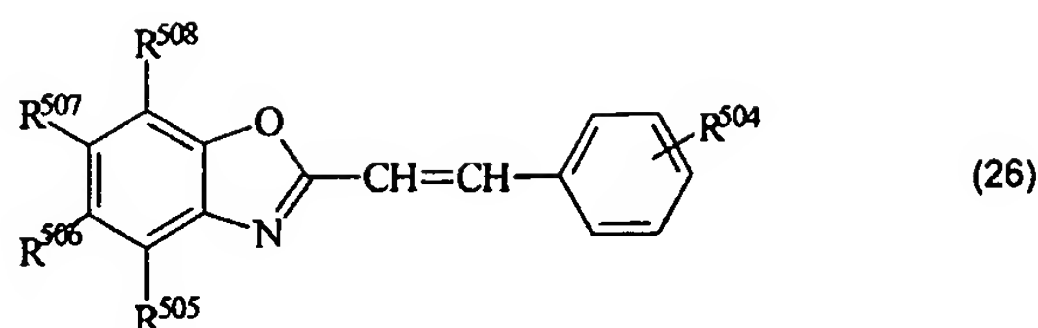


15

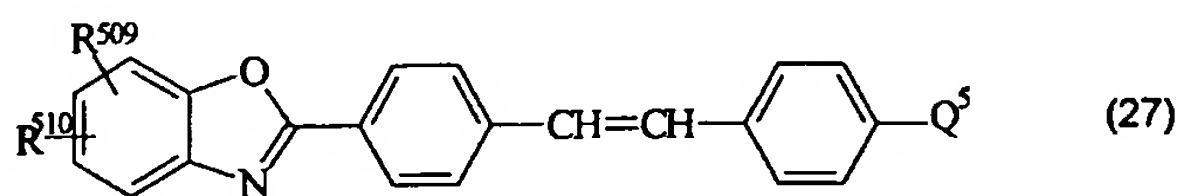
preferably



or one group R⁵⁰³ in each ring is 2-methyl and the other R⁵⁰³ is H and Q⁴ is
 20 -CH=CH-; or one group R⁵⁰³ in each ring is 2-C(CH₃)₃ and the other R⁵⁰³ is H;
 wherein the compound has a trans-coplanar orientation or cis-coplanar
 orientation, preferably a trans-coplanar orientation;

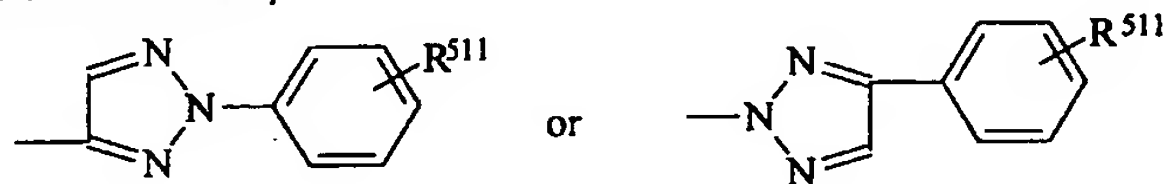


wherein R⁵⁰⁴ is CN, Cl, COO-C₁-C₃₀alkyl or phenyl; R⁵⁰⁵ and R⁵⁰⁶ are the
atoms required to form a fused benzene ring or R⁵⁰⁶ and R⁵⁰⁸, independently,
5 are H or C₁-C₃₀alkyl; and R⁵⁰⁷ is H, C₁-C₃₀alkyl or phenyl; wherein the
compound has a trans-coplanar orientation or cis-coplanar orientation; preferably
R⁵⁰⁴ is a 4-phenyl group and each of R⁵⁰⁵ to R⁵⁰⁸ is H; wherein the compound
has a trans-coplanar orientation; and



10

wherein R⁵⁰⁹ denotes H, Cl, alkyl with 1 to 30 carbon atoms, cyclohexyl,
phenylalkyl with 1 to 3 carbon atoms in the alkyl part, phenyl or alkoxy with 1 to
30 carbon atoms, R⁵¹⁰ denotes H or alkyl with 1 to 30 carbon atoms, and Q⁵
15 denotes a radical;

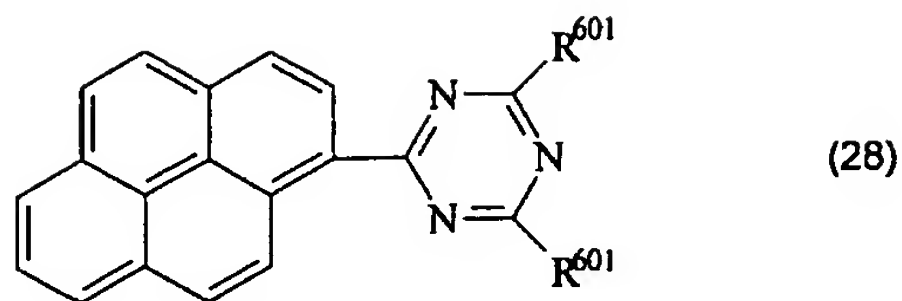


wherein R⁵¹¹ represents H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30
carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms, unsubstituted sulfamoyl
20 or sulfamoyl which is monosubstituted or disubstituted by alkyl or hydroxyalkyl
with 1 to 30 carbon atoms or represents alkylsulfonyl with 1 to 30 carbon atoms;
wherein the compound has a trans-coplanar orientation or cis-coplanar
orientation, preferably a trans-coplanar orientation.

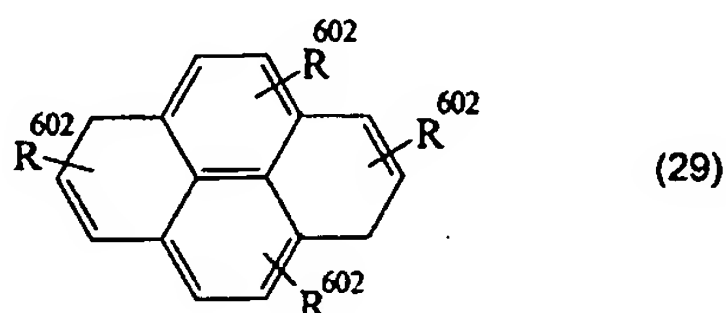
Suitable oxazoles include 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene, and
25 2-(4-methoxycarbonylstyryl)benzoxazole.

Pyrenes

Pyrenes useful in the present invention include those having formulae (28)
and (29):



wherein each R⁶⁰¹, independently, is C₁-C₃₀alkoxy; preferably methoxy; and



5

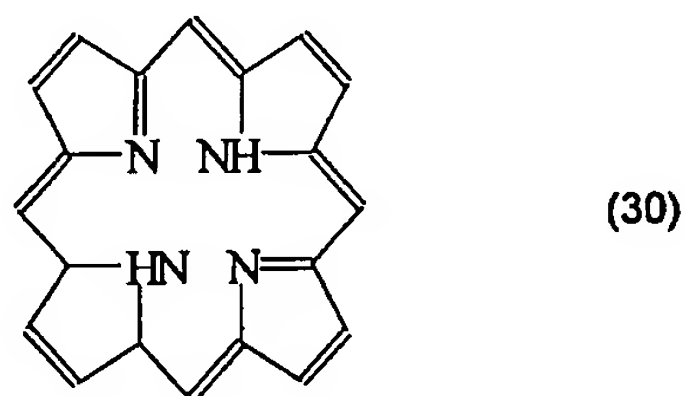
wherein each R⁶⁰², independently, is H, OH, or SO₃M, wherein M is as previously defined, sulfonated phenylamino, or anilino.

Suitable pyrenes include 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine (C.I. Fluorescent Brightener 179) with tradename Fluolite XMF, 8-hydroxy-1,3,6-pyrenetrisulfonic acid (D&C Green No.8), and 3-hydroxy-5,8,10-trisulphanilic pyrene.

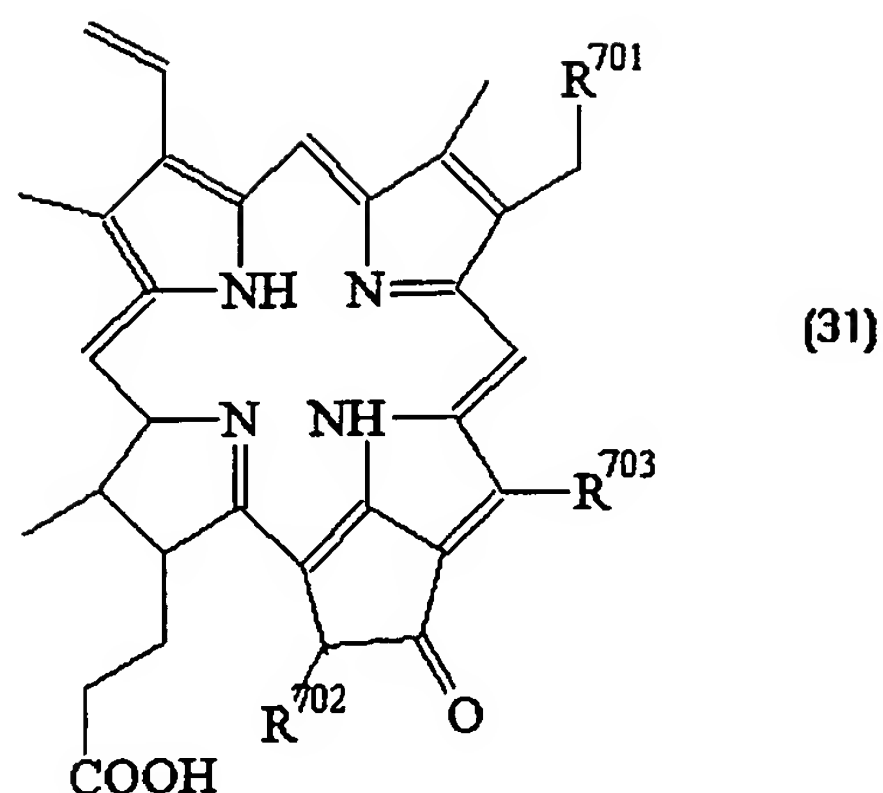
Porphyrins

Porphyrins useful in the present invention include those having formulae (30), (31), and (32):

15

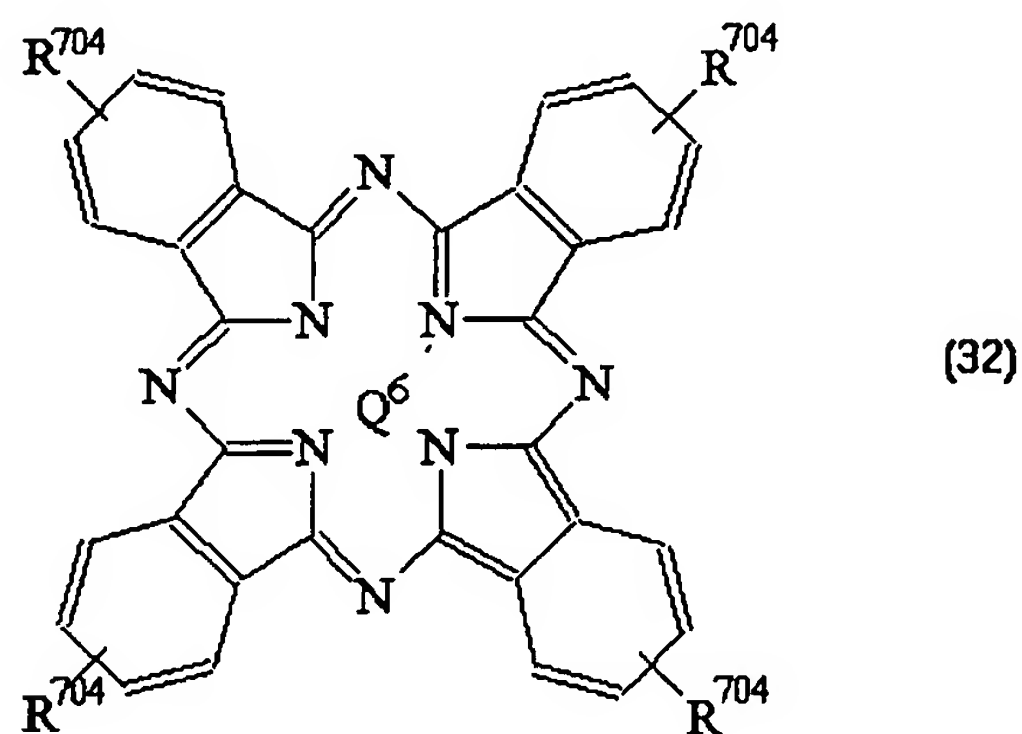


34



wherein R^{701} is CH_3 or CHO , R^{702} is H or $\text{COOC}_1\text{-C}_{30}$ alkyl, and R^{703} is H or an alkyl group having 1 to 30 carbons; and

5



wherein each R^{704} , independently, is H , SO_3M , COOM , OSO_3M , or $\text{OPO}(\text{OH})\text{OM}$, wherein M is as previously defined, halide, or alkyl of 1 to 30 carbons; and Q^6 is Cu , Mg , Fe , Cr , Co , or mixtures thereof with cationic charges.

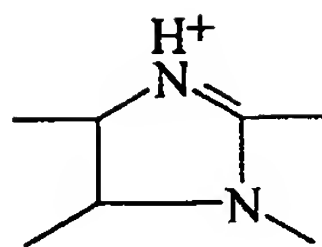
10

Suitable porphyrins include porphyrin available from Wako Chemicals and Copper II phthalocyanine available from Wako Chemicals.

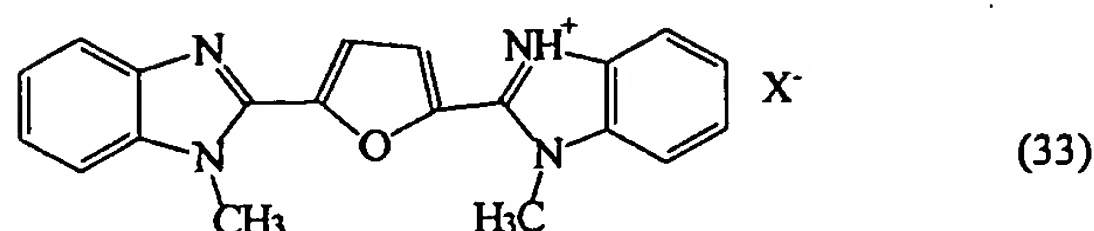
Imidazoles

Imidazoles are a class of compounds having the following base structure:

15



Imidazoles useful in the present invention include those having formulae
 5 (33):



wherein X^- is as previously defined.

10 Suitable imidazoles include those with tradename of C.I. Fluorescence Brightener 352, or Uvtext AT available from Ciba Speciality Chemical.

HERBAL EXTRACT

Herbal extracts useful as encompassed material herein include those which are water soluble and those which are water insoluble. Useful herbal extracts
 15 herein include: Polygonum multiflori Extract, Houttuynia cordate extract, Phellodendron Bark extract, melilot extract, white dead nettle extract, licorice root extract, herbaceous peony extract, soapwort extract, dishcloth gourd extract, cinchona extract, creeping saxifrage extract, Sophora angustifolia extract, candock extract, common fennel extract, primrose extract, rose extract,
 20 Rehmannia glutinosa extract, lemon extract, shikon extract, aloe extract, iris bulb extract, eucalyptus extract, field horsetail extract, sage extract, thyme extract, tea extract, laver extract, cucumber extract, clove extract, raspberry extract, melissa extract, ginseng extract, carrot extract, horse chestnut extract, peach extract, peach leaf extract, mulberry extract, cornflower extract, hamamelis extract,
 25 placenta extract, thymus extract, silk extract, algae extract, althea extract, angelica dahurica extract, apple extract, apricot kernel extract, arnica extract, Artemisia capillaris extract, astragal extract, balm mint extract, perilla extract, birch bark extract, bitter orange peel extract, Thea sinensis extract, burdock root extract, burnet extract, butcherbroom extract, Stephania cepharantha extract,
 30 matricaria extract, chrysanthemum flower extract, citrus unshiu peel extract, cnidium extract, coix seed extract, coltsfoot extract, comfrey leaf extract, crataegus extract, evening primrose oil, gambir extract, ganoderma extract,

gardenia extract, gentian extract, geranium extract, ginkgo extract, grape leaf extract, crataegus extract, henna extract, honeysuckle extract, honeysuckle flower extract, hoelen extract, hops extract, horsetail extract, hydrangea extract, hypericum extract, isodonis extract, ivy extract, Japanese angelica extract, Japanese coptis extract, juniper extract, jujube extract, lady's mantle extract, lavender extract, lettuce extract, licorice extract, linden extract, lithospermum extract, loquat extract, luffa extract, malloti extract, mallow extract, calendula extract, moutan bark extract, mistletoe extract, mukurossi extract, mugwort extract, mulberry root extract, nettle extract, nutmeg extract, orange extract, parsely extract, hydrolyzed conchiorin protein, peony root extract, peppermint extract, philodendron extract, pine cone extract, platycodon extract, polygonatum extract, rehmannia extract, rice bran extract, rhubarb extract, rose fruit extract, rosemary extract, royal jelly extract, safflower extract, saffron crocus extract, sambucus extract, saponaria extract, Sasa albo marginata extract, Saxifraga stolonifera extract, scutellaria root extract, Cortinellus shiitake extract, lithospermum extract, sophora extract, laurel extract, calamus root extract, swertia extract, thyme extract, linden extract, tomato extract, turmeric extract, uncaria extract, watercress extract, logwood extract, grape extract, white lily extract, rose hips extract, wild thyme extract, witch hazel extract, yarrow extract, yeast extract, yucca extract, zanthoxylum extract, and mixtures thereof.

Commercially available herbal extracts useful herein include Polygonum multiflori extracts which are water soluble, and available from Institute of Occupational Medicine, CAPM, China National Light Industry, and Maruzen, and other herbal extracts listed above available from Maruzen.

Useful silicone compounds, humectants, and additional conditioning agents for encompassed material are the same as those exemplified in other portions of the specification. The components herein, however, are substantially retained within the breakable visible particles, and are substantially not dissolved in the bulk of the present composition under normal shelf conditions.

Particularly useful commercially available breakable visible particles herein are those with tradenames Unisphere and Unicerin available from Induchem AG (Switzerland). Unisphere and Unicerin particles are made of microcrystalline cellulose, hydroxypropyl cellulose, lactose, vitamins, pigments, and proteins. Upon use, the Unisphere and Unicerin particles can be disintegrated with very little shear on the hand with the fingers with practically no

resistance, and readily dissolve in the composition.

AQUEOUS CARRIER

The compositions of the present invention comprise an aqueous. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

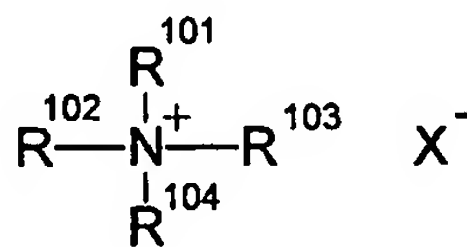
Carriers useful in the present invention include water and water solutions of lower alkyl alcohols. Lower alkyl alcohols useful herein are monohydric alcohols having 1 to 6 carbons, more preferably ethanol and isopropanol.

Preferably, the aqueous carrier is substantially water. Deionized water is preferably used. Water from natural sources including mineral cations can also be used, depending on the desired characteristic of the product. The compositions of the present invention comprise at least about 70%, preferably at least about 80% water.

QUATERNARY COMPOUND

The hair conditioning composition of the present invention may further comprise a quaternary compound. The quaternary compound contributes making the layered gel structure. The quaternary compound is comprised at a level of preferably from about 0.5% to about 5%, more preferably from about 1% to about 3% by weight of the composition.

Among the quaternary compounds useful herein are those corresponding to the general formula (I):



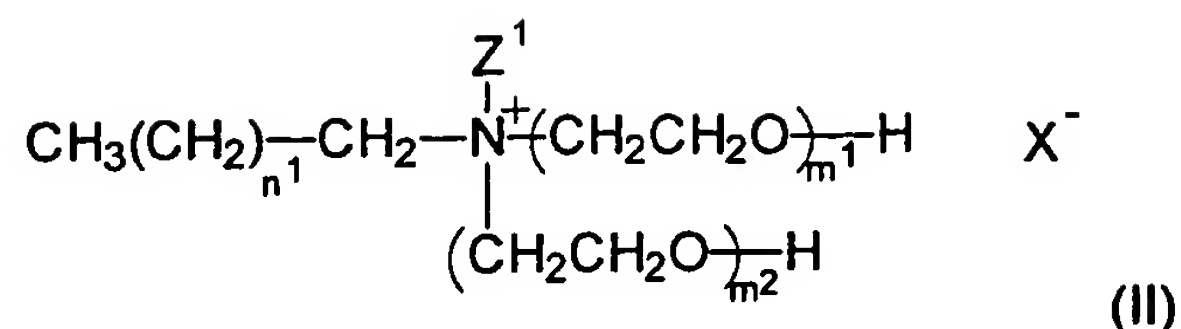
(I)

wherein at least one of R^{101} , R^{102} , R^{103} and R^{104} is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R^{101} , R^{102} , R^{103} and R^{104} are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain

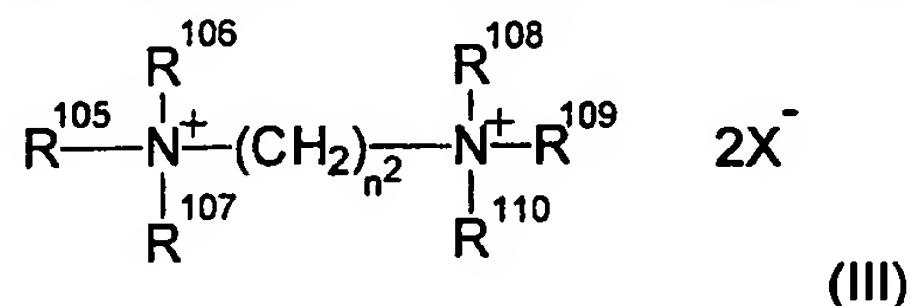
aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R^{101} , R^{102} , R^{103} and R^{104} are independently selected from C_1 to about C_{22} alkyl. Nonlimiting examples of quaternary compounds useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

Among the quaternary compounds of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons. Nonlimiting examples of such preferred quaternary compounds include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo Kasei; cetyl trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, di(behenyl/arachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl propyleneglycol phosphate dimethyl ammonium chloride, stearyl amidopropyl dimethyl benzyl ammonium chloride, stearyl amidopropyl dimethyl (myristylacetate) ammonium chloride, and N-(stearyl colamino formyl methy) pyridinium chloride.

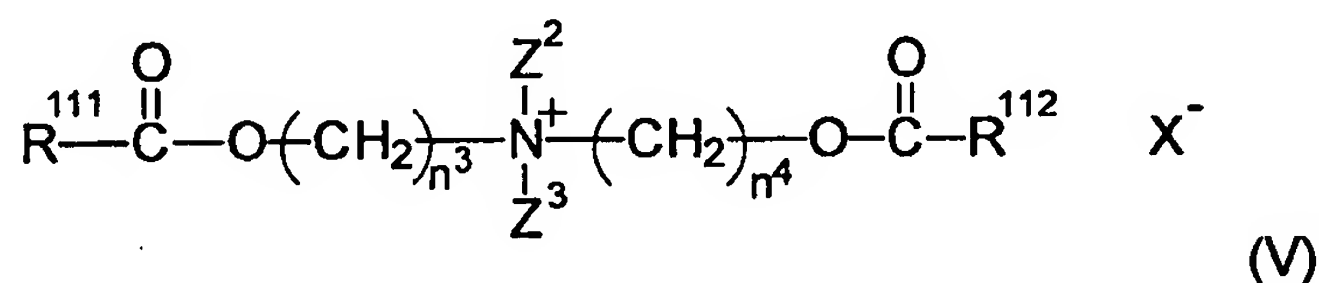
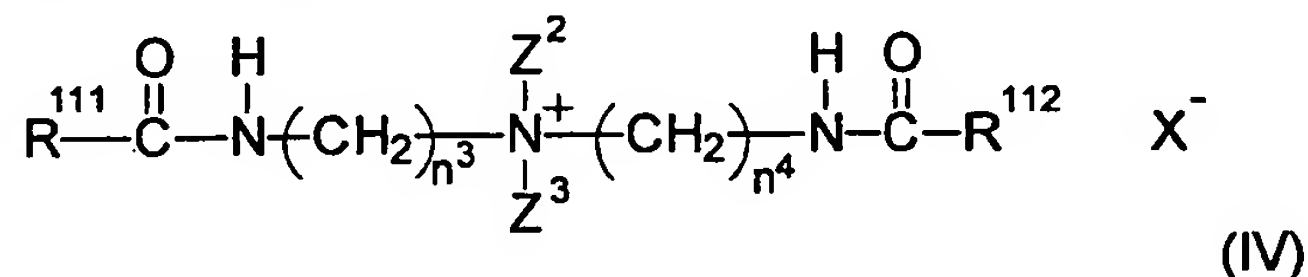
Also preferred as quaternary compounds are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R^{101} - R^{104} radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C_1 - C_3 alkoxy), polyoxyalkylene (preferably C_1 - C_3 polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VIII) below:



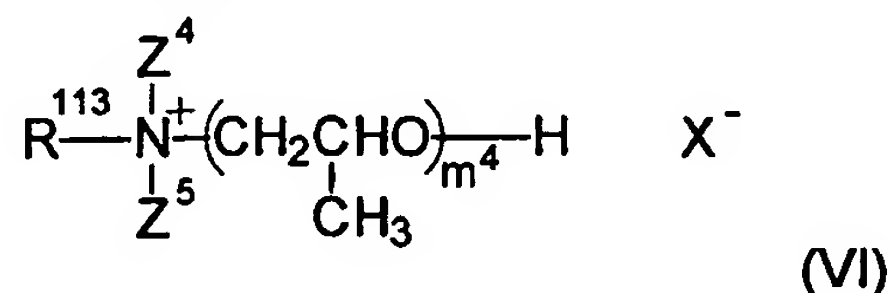
wherein n^1 is from 8 to about 28, m^1+m^2 is from 2 to about 40, Z^1 is a short chain alkyl, preferably a C_1 - C_3 alkyl, more preferably methyl, or $(\text{CH}_2\text{CH}_2\text{O})_{m^3}\text{H}$ wherein $m^1+m^2+m^3$ is up to 60, and X is a salt forming anion as defined above;



wherein n^2 is 1 to 5, one or more of R^{105} , R^{106} , and R^{107} are independently an C_1 - C_{30} alkyl, the remainder are $\text{CH}_2\text{CH}_2\text{OH}$, one or two of R^{108} , R^{109} , and R^{110} are independently an C_1 - C_{30} alkyl, and remainder are $\text{CH}_2\text{CH}_2\text{OH}$, and X is a salt forming anion as mentioned above;

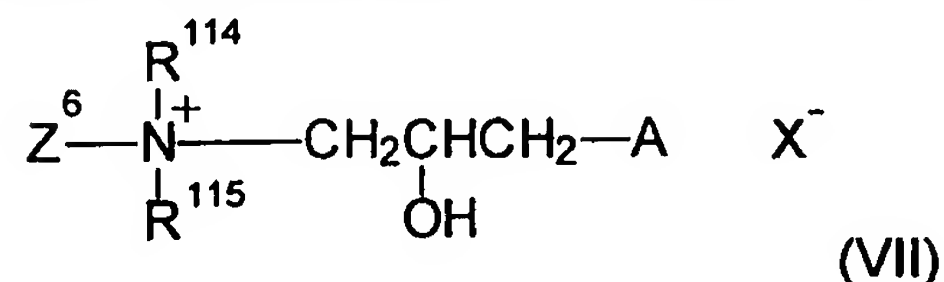


wherein, independently for formulae (IV) and (V), Z^2 is an alkyl, preferably C_1 - C_3 alkyl, more preferably methyl, and Z^3 is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, n^3 and n^4 independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R^{111} and R^{112} , independently, are substituted or unsubstituted hydrocarbyls, C_{12} - C_{20} alkyl or alkenyl, and X is a salt forming anion as defined above;

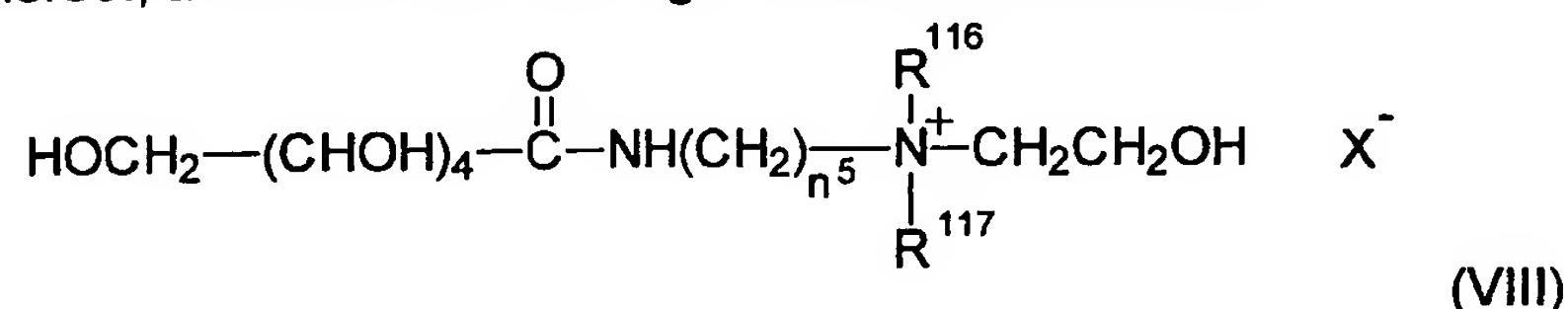


wherein R^{113} is a hydrocarbyl, preferably a C_1 - C_3 alkyl, more preferably methyl, Z^4 and Z^5 are, independently, short chain hydrocarbyls, preferably C_2 - C_4 alkyl or alkenyl, more preferably ethyl, m^4 is from 2 to about 40, preferably from about 7

to about 30, and X is a salt forming anion as defined above;



wherein R^{114} and R^{115} , independently, are C_1 - C_3 alkyl, preferably methyl, Z^6 is a C_{12} - C_{22} hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;



wherein n^5 is 2 or 3, R^{116} and R^{117} , independently are C_1 - C_3 hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-72, quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamido ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkyloyl ethyl hydroxyethylmonium salt, dialkyloyl ethyldimonium salt, and mixtures thereof; for example, commercially available under the following tradenames; VARISOFT 110, VARISOFT 222, VARIQUAT K1215 and VARIQUAT 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265

from ICI Americas.

HUMECTANT

The compositions of the present invention may contain a humectant. The humectants herein are selected from the group consisting of polyhydric alcohols, water soluble alkoxyated nonionic polymers, and mixtures thereof. The humectants herein are preferably used at levels by weight of the composition of from about 0.1% to about 20%, more preferably from about 0.5% to about 5%.

Polyhydric alcohols useful herein include glycerin, sorbitol, propylene glycol, butylene glycol, hexylene glycol, ethoxylated glucose, 1, 2-hexane diol, hexanetriol, dipropylene glycol, erythritol, trehalose, diglycerin, xylitol, maltitol, maltose, glucose, fructose, sodium chondroitin sulfate, sodium hyaluronate, sodium adenosin phosphate, sodium lactate, pyrrolidone carbonate, glucosamine, cyclodextrin, and mixtures thereof.

Water soluble alkoxyated nonionic polymers useful herein include polyethylene glycols and polypropylene glycols having a molecular weight of up to about 1000 such as those with CTFA names PEG-200, PEG-400, PEG-600, PEG-1000, and mixtures thereof.

Commercially available humectants herein include: glycerin with tradenames STAR and SUPEROL available from The Procter & Gamble Company, CRODEROL GA7000 available from Croda Universal Ltd., PRECERIN series available from Unichema, and a same tradename as the chemical name available from NOF; propylene glycol with tradename LEXOL PG-865/855 available from Inolex, 1,2-PROPYLENE GLYCOL USP available from BASF; sorbitol with tradenames LIPONIC series available from Lipo, SORBO, ALEX, A-625, and A-641 available from ICI, and UNISWEET 70, UNISWEET CONC available from UPI; dipropylene glycol with the same tradename available from BASF; diglycerin with tradename DIGLYCEROL available from Solvay GmbH; xylitol with the same tradename available from Kyowa and Eizai; maltitol with tradename MALBIT available from Hayashibara, sodium chondroitin sulfate with the same tradename available from Freeman and Bioiberica, and with tradename ATOMERGIC SODIUM CHONDROITIN SULFATE available from Atomergic Chemetals; sodium hyaluronate with tradenames ACTIMOIST available from Active Organics, AVIAN SODIUM HYALURONATE series available from Intergen, HYALURONIC ACID Na available from Ichimaru Pharcos; sodium adenosin phosphate with the same

tradename available from Asahikasei, Kyowa, and Daiichi Seiyaku; sodium lactate with the same tradename available from Merck, Wako, and Showa Kako, cyclodextrin with tradenames CAVITRON available from American Maize, RHODOCAP series available from Rhone-Poulenc, and DEXPEARL available from Tomen; and polyethylene glycols with the tradename CARBOWAX series available from Union Carbide.

ADDITIONAL CONDITIONING AGENTS

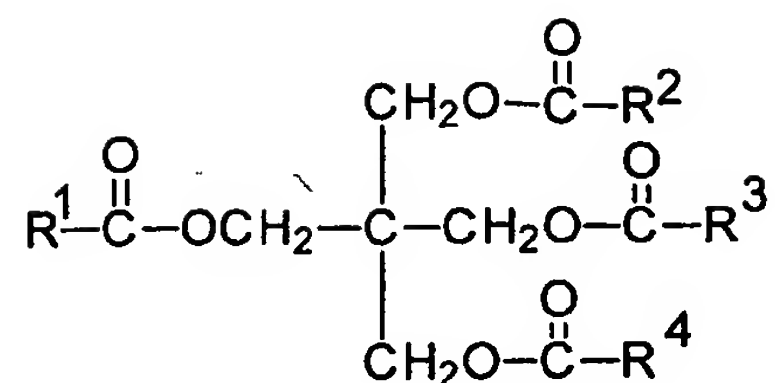
The compositions of the present invention may contain by weight from about 0.01% to about 20.0%, preferably from about 1.0% to about 15.0%, and more preferably from about 2.0% to about 10.0%, of additional conditioning agents. Suitable additional conditioning agents useful herein include high molecular weight ester oils, additional oily compounds, silicone compounds, and nonionic polymers.

High Molecular Weight Ester Oil

The compositions of the present invention may further comprise a high molecular weight ester oil selected from the group consisting of pentaerythritol ester oils, trimethylol ester oils, poly α -olefin oils, citrate ester oils, glyceryl ester oils, and mixtures thereof. The high molecular weight ester oils useful herein are those which are water-insoluble, and are in liquid form at 25°C. As used herein, the term "water-insoluble" means the compound is substantially not soluble in water at 25°C; when the compound is mixed with water at a concentration by weight of above 1.0%, preferably at above 0.5%, the compound is temporarily dispersed to form an unstable colloid in water, then is quickly separated from water into two phases.

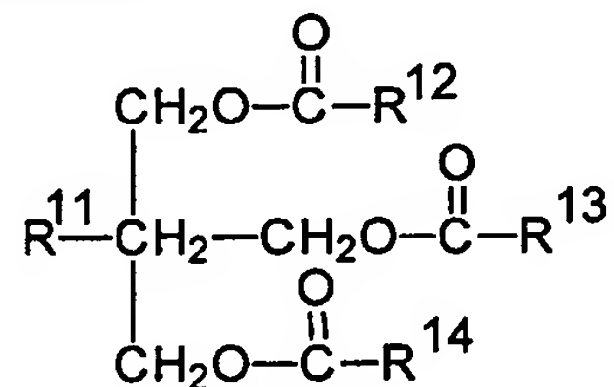
The high molecular weight ester oil herein provides moisturized feel, smooth feel, and manageability control to the hair when the hair is dried, yet not leave the hair feeling greasy. Thus, with the addition of the high molecular weight ester oil, obtained is a composition that can provide particularly suitable conditioning benefits both when the hair is wet and also after it has dried. The high molecular weight ester oil may be comprised at a level of preferably from about 0.2% to about 10%, more preferably from about 0.5% to about 5% by weight of the composition.

Pentaerythritol ester oils useful herein are those of the following formula having a molecular weight of at least 800:



wherein R¹, R², R³, and R⁴, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R¹, R², R³, and R⁴, independently, are branched, straight, saturated, or unsaturated alkyl groups having from about 8 to about 22 carbons. More preferably, R¹, R², R³ and R⁴ are defined so that the molecular weight of the compound is from about 800 to about 1200.

Trimethylol ester oils useful herein are those of the following formula having a molecular weight of at least 800:



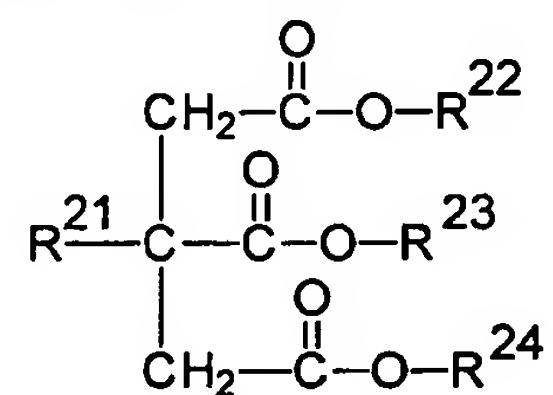
wherein R¹¹ is an alkyl group having from 1 to about 30 carbons, and R¹², R¹³, and R¹⁴, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R¹¹ is ethyl and R¹², R¹³, and R¹⁴, independently, are branched, straight, saturated, or unsaturated alkyl groups having from 8 to about 22 carbons. More preferably, R¹¹, R¹², R¹³ and R¹⁴ are defined so that the molecular weight of the compound is from about 800 to about 1200.

Poly α -olefin oils useful herein are those derived from 1-alkene monomers having from about 6 to about 16 carbons, preferably from about 6 to about 12 carbons atoms. Nonlimiting examples of 1-alkene monomers useful for preparing the poly α -olefin oils include 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, branched isomers such as 4-methyl-1-pentene, and mixtures thereof. Preferred 1-alkene monomers useful for preparing the poly α -olefin oils are 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and mixtures thereof. Poly α -olefin oils useful herein further have a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, and a polydispersity of no more than

about 3.

Poly α -olefin oils having a molecular weight of at least about 800 are useful herein. Such high molecular weight poly α -olefin oils are believed to provide long lasting moisturized feel to the hair. Poly α -olefin oils having a molecular weight of less than about 800 are useful herein. Such low molecular weight poly α -olefin oils are believed to provide a smooth, light, clean feel to the hair.

Citrate ester oils useful herein are those having a molecular weight of at least about 500 having the following formula:

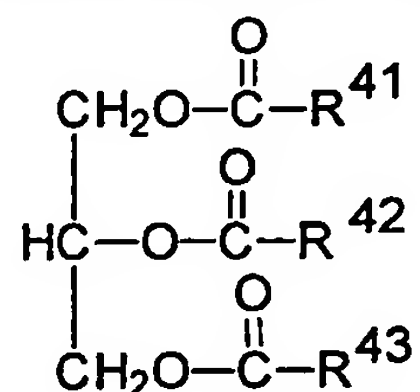


10

wherein R^{21} is OH or CH_3COO , and R^{22} , R^{23} , and R^{24} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R^{21} is OH, and R^{22} , R^{23} , and R^{24} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, R^{21} , R^{22} , R^{23} and R^{24} are defined so that the molecular weight of the compound is at least about 800.

15

Glyceryl ester oils useful herein are those having a molecular weight of at least about 500 and having the following formula:



20

wherein R^{41} , R^{42} , and R^{43} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R^{41} , R^{42} , and R^{43} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, R^{41} , R^{42} , and R^{43} are defined so that the molecular weight of the compound is at least about 800.

25

Particularly preferable high molecular weight ester oils are pentaester oils

and trimethylol ester oils.

Particularly useful pentaerythritol ester oils and trimethylol ester oils herein include pentaerythritol tetraisostearate, pentaerythritol tetraoleate, trimethylolpropane triisostearate, trimethylolpropane trioleate, and mixtures thereof. Such compounds are available from Kokyo Alcohol with tradenames KAKPTI, KAKTTI, and Shin-nihon Rika with tradenames PTO, ENUJERUBU TP3SO.

Particularly useful poly α -olefin oils herein include polydecenes with tradename PURESYN 6 having a molecular weight of about 500 and PURESYN 100 having a molecular weight of over 3000 available from Mobil Chemical Co.

Particularly useful citrate ester oils herein include triisocetyl citrate with tradename CITMOL 316 available from Bernel, triisostearyl citrate with tradename PELEMOL TISC available from Phoenix, and trioctyldodecyl citrate with tradename CITMOL 320 available from Bernel.

Particularly useful glyceryl ester oils herein include triisostearin with tradename SUN ESPOL G-318 available from Taiyo Kagaku, triolein with tradename CITHROL GTO available from Croda Surfactants Ltd., trilinolein with tradename EFADERMA-F available from Vevy, or tradename EFA-GLYCERIDES from Brooks.

Additional Oily Compound

Additional oily compounds useful herein include fatty alcohols and their derivatives, fatty acids and their derivatives, and hydrocarbons. The additional oily compounds useful herein may be volatile or nonvolatile, and have a melting point of not more than about 25C. Without being bound by theory, it is believed that, the additional oily compounds may penetrate into the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The additional oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the additional oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated

alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

5 The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic
10 acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

 The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils,
15 glyceryl ester oils, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl
20 isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, isopropyl isostearate, ethyl isostearate, methyl isostearate and Oleth-2. Bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils and glyceryl ester oils useful herein are those which have a molecular weight of less than about 800, preferably less than
25 about 500.

 The hydrocarbons useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from
30 about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C₂₋₈ alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described
35 above. The branched chain polymers can have substantially higher chain

lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, poly α -olefin oils such as isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available fatty alcohols and their derivatives useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from Shin Nihon Rika, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol. Commercially available bulky ester oils useful herein include: trimethylolpropane tricaprilate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co. Commercially available hydrocarbons useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA), and polydecene with tradename PURESYN 6 from Mobil Chemical Co.

Silicone Compounds

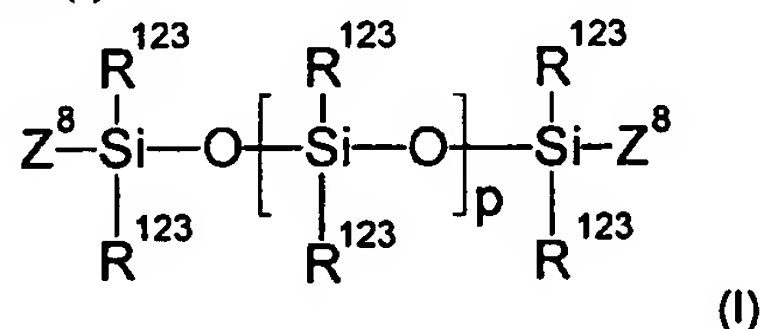
The compositions of the present invention may contain a silicone compound. The silicone compounds useful herein include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compounds herein may be made by any suitable method known in

the art, including emulsion polymerization. The silicone compounds may further be incorporated in the present composition in the form of an emulsion, wherein the emulsion is made by mechanical mixing, or in the stage of synthesis through emulsion polymerization, with or without the aid of a surfactant selected from anionic surfactants, nonionic surfactants, cationic surfactants, and mixtures thereof.

The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970. Silicone compound of high molecular weight may be made by emulsion polymerization. Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compound is preferably included in the composition at a level by weight from about 0.01% to about 20%, more preferably from about 0.05% to about 10%.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



wherein R^{123} is alkyl or aryl, and x is an integer from about 7 to about 8,000. Z^8 represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R^{123}) or at the ends of the siloxane chains Z^8 can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable Z^8 groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R^{123} groups on the silicon atom may represent the same group or different groups.

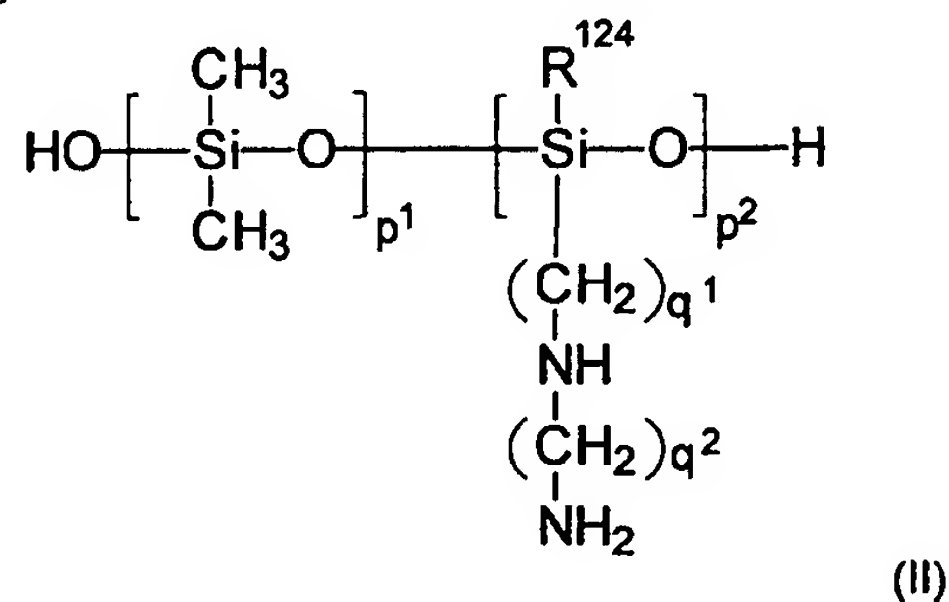
Preferably, the two R^{123} groups represent the same group. Suitable R^{123} groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their Viscasil® and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)

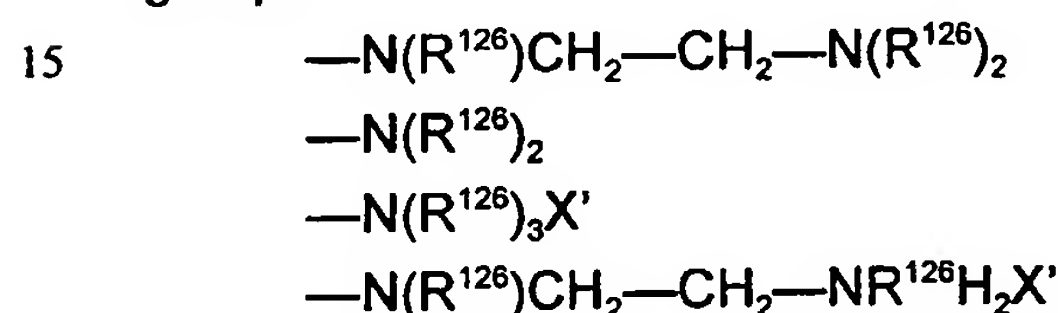


wherein R^{124} is H, CH_3 or OH, p^1 , p^2 , q^1 and q^2 are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the
5 formula (III)



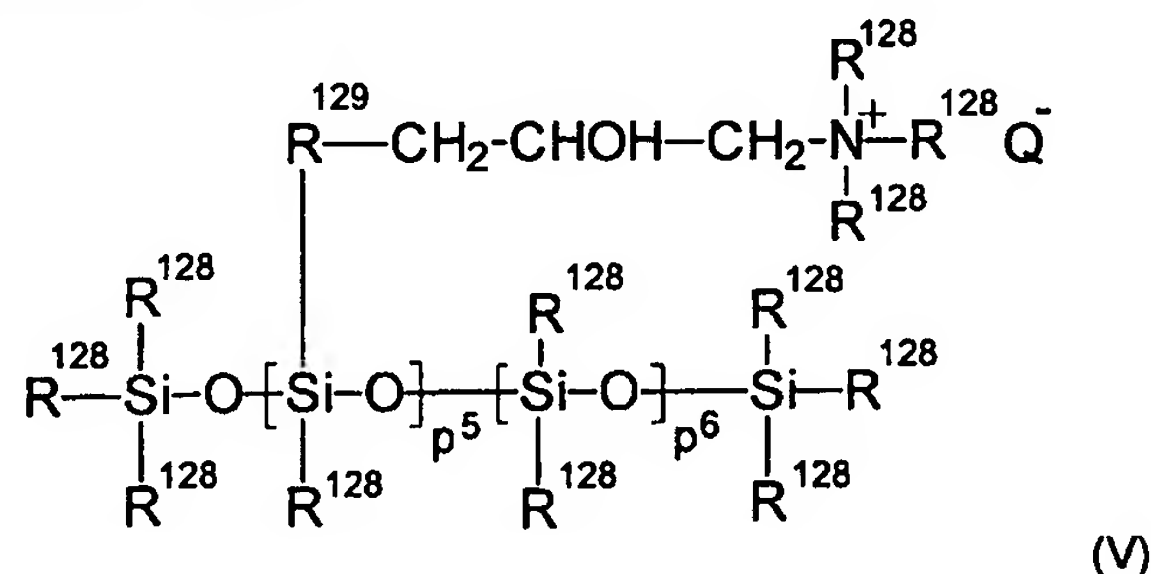
in which G is chosen from the group consisting of hydrogen, phenyl, OH, C_1 - C_8 alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum $p^3 + p^4$ is a number
10 from 1 to 2,000 and preferably from 50 to 150, p^3 being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and p^4 being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R^{125} is a monovalent radical of formula $C_{q^3}H_{2q^3}L$ in which q^3 is an integer from 2 to 8 and L is chosen from the groups



in which R^{126} is chosen from the group consisting of hydrogen, phenyl, benzyl, a
20 saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and X' denotes a halide ion.

An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone" wherein R^{124} is CH_3 .

25 Other amino substituted silicone polymers which can be used are represented by the formula (V):



where R^{128} denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R^{129} denotes

a hydrocarbon radical, preferably a C_1 - C_{18} alkylene radical or a C_1 - C_{18} , and more preferably C_1 - C_8 , alkyleneoxy radical; Q^- is a halide ion, preferably chloride; p^5 denotes an average statistical value from 2 to 20, preferably from 2 to 8; p^6 denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56".

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston. "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984, provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer *et al.*, issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of

crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl™ from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp. 204-308, John Wiley & Sons, Inc., 1989.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(\text{CH}_3)_3\text{SiO}_{0.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average

thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before,
 5 however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to
 10 about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

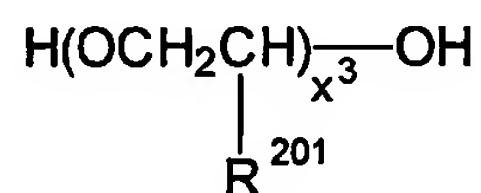
Commercially available silicone compounds which are useful herein include Dimethicone with tradename D-130, cetyl Dimethicone with tradename DC2502, stearyl Dimethicone with tradename DC2503, emulsified polydimethyl
 15 siloxanes with tradenames DC1664 and DC1784, and alkyl grafted copolymer silicone emulsion with tradename DC2-2845; all available from Dow Corning Corporation, and emulsion polymerized Dimethiconol available from Toshiba Silicone as described in GB application 2,303,857.

Nonionic Polymer

20 Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with
 25 tradename KLUCCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Hercules. Other suitable nonionic polymers are ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

Polyalkylene Glycol

30 The polyalkylene glycols are characterized by the general formula:



wherein R²⁰¹ is selected from the group consisting of H, methyl, and mixtures thereof. When R²⁰¹ is H, these materials are polymers of ethylene oxide, which

are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R^{201} is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R^{201} is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, x3 has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably from about 3500 to about 15,000.

Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

Polyethylene glycol polymers useful herein are PEG-2M wherein R^{201} equals H and x3 has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein R^{201} equals H and x3 has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein R^{201} equals H and x3 has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein R^{201} equals H and x3 has an average value of about 9,000 (PEG 9-M is also known as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein R^{201} equals H and x3 has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

OTHER ADDITIONAL COMPONENTS

The compositions of the present invention may include other additional components, which may be selected by the artisan according to the desired characteristics of the final product and which are suitable for rendering the compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such other additional components generally are used individually at levels from about 0.001% to about 10.0%, preferably from about 0.01% to about 5.0% by weight of the composition.

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as hydrolysed collagen with tradename Peptin 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche,

panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, antidandruff agents such as zinc pyridinethione; and mixtures thereof.

METHOD OF MAKING

The hair conditioning composition of the present invention can be made by any means which provide the composition with a layered gel structure, and thereby the DSC profile of the composition shows substantially no peaks larger than about 3 mJ/mg from about 40°C to about 55°C. The composition of the present invention is preferably made by the steps of forming the layered gel structure, then blending with the breakable visible particles via a static mixer such as those supplied by BRAN and LUEBBE. Preferably, the breakable visible particles are premixed with a liquid carrier having a viscosity of more than about 1000 cs. In one preferred embodiment, the breakable visible particles are premixed with a non-volatile silicone fluid.

When the composition contains quaternary compounds, the layered gel structure is preferably made by the sub-steps of:

- (1) forming a first mixture comprising the high melting point compound, the emulsifying agent, and the aqueous carrier at a first temperature of at least about 75°C;
- (2) cooling the first mixture by at least 5°C to a second temperature of from about 50°C to about 75°C; and
- (3) adding the quaternary compound, when included, to the product of step (2) while maintaining the second temperature.

Forming a First Mixture

The first step comprises forming a first mixture comprising the high

melting point compound, the emulsifying agent, and water at a first temperature of at least about 75°C. The first mixture is made homogeneous by a suitable means such as stirring. Certain compounds in the hair conditioning composition are not contained in the first mixture. Compounds not contained are the quaternary compound, and, if present, volatile and heat-sensitive compounds. Any other compounds of the present composition are typically included in the first mixture. The first temperature for making the first mixture is at least about 75°C, preferably from about 75°C to about 85°C.

Cooling the First Mixture

The second step comprises cooling the first mixture by at least 5°C to a second temperature of from about 50°C to about 75°C. The cooling can be done by any suitable means, for example by heat exchangers, or jacket cooling instruments. The second temperature is from about 50°C to about 75°C, preferably from about 55°C to about 65°C, more preferably from about 55°C to about 60°C. The second temperature is higher than the melting point of the high melting point compound.

Typically, the second temperature is no more than 5°C higher, preferably from about 2°C to 5°C higher than the thickening temperature of the first mixture. The thickening temperature is a point in which the rheology of a composition significantly changes, i.e., the first mixture becomes dramatically and significantly viscous. Such phenomena are well recognized by the artisan for compositions which contain high melting point compounds.

Adding the Quaternary Compound

The third step comprises adding the quaternary compound, when included, to the product of the second step while maintaining the second temperature. Such addition of the quaternary compound is typically done under stirring. Without being bound by theory, it is believed that, by adding the quaternary compound at the second temperature, the phase of the composition is transformed to a layered gel structure. Certain compounds which are not contained in the first mixture such as volatile and heat-sensitive compounds can be included at the third step, or after the product of the third step is cooled to room temperature.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

The compositions of the present invention are suitable for rinse-off products and leave-on products, and are particularly useful for making products in the form of emulsion, cream, gel, spray, or mousse.

Examples 1 through 6 are hair conditioning compositions of the present invention which are particularly useful for rinse-off use.

Compositions

Components	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Cetyl Alcohol *1	4.5	4.5	4.0	4.0	4.5	4.5
Stearyl Alcohol *2	2.5	2.5	2.0	2.5	2.5	2.5
Behenyl Alcohol *3	-	1.0	-	1.0	0.5	-
Stearamidopropyl Dimethylamine *4	2.0	2.0	2.0	2.0	1.0	0.5
L-Glutamic Acid *5	0.32	0.64	0.8	0.6	0.64	0.64
Stearamidopropyl betaine *6	-	-	-	-	1.0	1.0
Behenylamidopropyl betaine	-	-	-	-	-	1.0
Breakable visible particle 1 *7	0.2	-	-	-	0.1	
Breakable visible particle 2 *8	-	0.2	-	0.1	0.1	-
Breakable visible particle 3 *9	-	-	0.1	0.1	-	0.1
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate *10	-	1.0	-	-	-	1.0
Distearamidoethyl hydroxyethylmonium methosulfate	-	-	1.0	1.0	1.0	-
Hydroxyethyl Cellulose *11	-	-	-	-	0.5	0.1
Polyoxyethylene Glycol *12	-	0.1	0.1	-	-	-
Pentaerythritol Tetraisostearate *13	-	-	0.5	-	-	-
Pentaerythritol Tetraoleate *14	-	1.0	-	0.5	-	-
Trimethylolpropane Trioleate *15	-	-	0.5	0.5	1.0	1.0
Trimethylolpropane Triisostearate *16	-	-	-	-	-	1.0
Preservatives	0.04	0.04	0.04	0.04	0.04	0.04

Benzyl alcohol	0.4	0.4	0.4	0.4	0.4	0.4
Perfume	0.25	0.25	0.25	0.25	0.25	0.25
Silicone Blend *17	4.2	2.5	4.2	2.5	2.5	2.5
Silicone Emulsion *18	-	-	-	0.5	0.5	0.5
Hydrolyzed collagen *19	0.01	0.01	0.01	0.01	0.01	0.01
Vitamin E *20	0.01	0.01	0.01	0.01	0.01	0.01
Panthenol *21	0.03	0.03	0.03	0.03	0.03	0.03
Panthenyl Ethyl Ether *22	0.25	0.25	0.25	0.25	0.25	0.25
Citric Acid *23	amount necessary to adjust pH 3-7					
Deionized Water	-----q.s. to 100%-----					

Definitions of Components

- *1 Cetyl Alcohol: Konol series obtained by Shin-Nihon Rika.
- *2 Stearyl Alcohol: Konol series obtained by Shin-Nihon Rika.
- *3 Behenyl Alcohol: 1-Docosanol (97%) obtained by Wako.
- 5 *4 Stearamidopropyl Dimethylamine: Amidoamine MPS obtained by Nikko.
- *5 *l*-Glutamic Acid: *l*-Glutamic acid (cosmetic grade) obtained by Ajinomoto.
- *6 Stearamidopropyl betaine: Rikabion A-700 available from Shin-Nihon Rika.
- *7 Breakable visible particle 1: Unispheres AGE-527 available from Induchem AG
- 10 *8 Breakable visible particle 2: Unispheres YE-501: available from Induchem AG
- *9 Breakable visible particle 3: Unicerin C-30 available from Induchem AG
- *10 Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate: Varisoft 110 obtained by Witco.
- 15 *11 Hydroxyethyl Cellulose: Available from Aqualon.
- *12 Polyoxyethyleneglycol: WSR N-10 obtained Amerchol.
- *13 Pentaerythritol Tetraisostearate: KAK PTI obtained by Kokyu alcohol.
- *14 Pentaerythritol Tetraoleate: Available from Shin-Nihon RiKa.
- *15 Trimethylolpropane Trioleate: Enujerubu TP3SO obtained by Shin-Nihon RiKa.
- 20 *16 Trimethylolpropane Triisostearate: KAK TTI obtained by Kokyu alcohol.
- *17 Silicone Blend: SE76 obtained by G.E.
- *18 Silicone Emulsion: X65-4829 obtained by Tosil/GE.
- *19 Hydrolyzed Collagen: Peptin 2000 obtained by Hormel.
- 25 *20 Vitamin E: Emix-d obtained by Eisai.

*21 Panthenol: Available from Roche.

*22 Panthenyl Ethyl Ether: Available from Roche.

*23 Citric Acid: Anhydrous Citric acid obtained by Haarman & Reimer.

Method of Preparation

5 The compositions of Examples 1 through 6 as shown above are prepared as follows: If included in the composition, polymeric materials such as hydroxyethyl cellulose, polyoxyethyleneglycol are dispersed in water at room temperature to make a copolymer solution. High melting point compounds, emulsifying agents, and the polymer solution, if present, are mixed and heated
10 up to the first temperature. The mixture thus obtained is cooled down to the second temperature, and the quaternary compound, if included, is added. The final mixture thus obtained is cooled below 55°C to make the first premix. In a separate container, the breakable visible particles, the Silicone Blend and, if included, the Silicone Emulsion, are blended with agitation to make the second
15 premix. The first and second premixes are blended via a static mixer and further cooled down to about 30°C.

A triblender and static mixer and/or mill can be used in each step, if necessary to disperse the materials.

20 Examples 1 through 6 are hair conditioning compositions of the present invention which are particularly useful for rinse-off use. These examples have many advantages. For example, they can further provide improved conditioning benefits to the hair such as smoothness, softness, anti-static and reduction of friction. The breakable visible particles readily disintegrate with little shear on the hand with the fingers.

25 It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

WHAT IS CLAIMED IS:

1. A hair conditioning composition comprising by weight:
 - (1) at least about 3% of a high melting point compound having a melting point of at least about 25°C;
 - (2) an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof;
 - 5 (3) a breakable visible particle comprising structural material selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof; and
 - 10 (4) an aqueous carrier;wherein the composition shows a DSC profile having substantially no peaks larger than about 3mJ/mg from about 40°C to about 55°C.
2. The hair conditioning composition according to Claim 1 wherein the emulsifying agent is selected from amines.
3. The hair conditioning composition according to Claim 2 wherein the amines are tertiary amido amines having an alkyl group of from about 12 to about 22 carbons.
4. The hair conditioning composition according to Claim 3 further comprising an acid selected from the group consisting of *l*-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, *l*-glutamic acid hydrochloride, tartaric acid, citric acid, and mixtures thereof; wherein the
5 molar ratio of the tertiary amido amine to the acid is from about 1 : 0.3 to about 1 : 2.
5. The hair conditioning composition according to Claim 2, 3, or 4 wherein the high melting point compound is selected from cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.
6. The hair conditioning composition according to Claim 1 wherein the composition further comprises a quaternary compound.

7. The hair conditioning composition according to Claim 6 wherein the quaternary compound is a hydrophilically substituted cationic surfactant selected from the group consisting of dialkylamido ethyl hydroxyethylmonium salt, dialkylamido ethyl dimonium salt, dialkoyl ethyl hydroxyethylmonium salt, dialkoyl ethyldimonium salt, and mixtures thereof.
8. A method of making the hair conditioning composition of Claim 1 comprising the steps of forming the layered gel structure, then adding the breakable visible particles by an in-line mixer.
9. The method of Claim 8 wherein forming the layered gel structure comprises the sub-steps of:
- (1) forming a first mixture comprising the high melting point compound, the emulsifying agent, and the aqueous carrier at a first temperature of at least about 75°C;
 - (2) cooling the first mixture by at least 5°C to a second temperature of from about 50°C to about 75°C; and
 - (3) adding the quaternary compound to the product of step (2) while maintaining the second temperature.
10. The method of Claim 9 wherein the second temperature is no more than 5°C higher than the thickening temperature of the product of the first mixture.

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/US 99/00018

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/06 A61K7/00 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 726 137 A (PATEL AMRIT ET AL) 10 March 1998 (1998-03-10) example 2 column 5 column 4, line 41-67 ---	1,6
Y	EP 0 795 317 A (WELLA AG) 17 September 1997 (1997-09-17) examples 22-24, 26-28, 31, 39 ---	1,6
A	US 5 468 496 A (TOUZAN PHILIPPE ET AL) 21 November 1995 (1995-11-21) examples 1-4 column 4, line 1-35 column 3, line 20-67 column 1, line 59-67 --- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

8 November 1999

Date of mailing of the international search report

22/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Sierra Gonzalez, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00018

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 218 (C-301), 5 September 1985 (1985-09-05) & JP 60 078907 A (KOBAYASHI KOOSEE), 4 May 1985 (1985-05-04) abstract ----	1-10
A	WO 97 23194 A (CHEIL JEDANG CORP ;KANG GIL SUNG (KR); KIM IN HO (KR); PARK HAE HO) 3 July 1997 (1997-07-03) page 5, line 3-5; claims 1,9,10 ----	1-10
A	WO 97 31616 A (NAKAMURA KIICHIRO ;YOKOGI JUNICHI (JP); MITSUMATSU ARATA (JP); PRO) 4 September 1997 (1997-09-04) page 3-7 page 10, line 31-34 page 11, line 1-28 page 17, line 28-32 examples 1-18 claims 1-9 -----	1-10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 00018

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-10 (partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
See FURTHER INFORMATION SHEET PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99 00018

FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

Continuation of Box I.2

Claims Nos.: 1-10 (partially)

It appears from the description as a whole and in particular from page 4, lines 6-8, page 5, line 35, page 6, line 1, page 37, lines 15-17 and page 56, lines 27-29, that the presence of a quaternary compound together with a high melting point compound in a composition forming a layered gel structure is an essential feature of the present application. These essential technical features are however not present in independent claims 1 and 8. Besides, the Applicant has not given enough information about how to make the layered gel structure when no quaternary compound is present. For this reasons claims 1 and 8 lack clarity and support according to Article 6 PCT taken in combination with Rule 6.3 (b) PCT (see also PCT Preliminary Examination Guidelines III.4.3).

Furthermore, claim 1 refers to a composition containing a high melting point compound having a melting point of at least about 25°C, such a composition presenting a particular structure, i.e. a layered gel, which is characterized by a certain DSC profile. The property of having a melting point of at least 25°C can be a property of many compounds. However, in the examples only three fatty alcohols, namely cetyl, stearyl and behenyl alcohol are used for this purpose, i.e. to form the so-called layered gel structure. It would seem that the disclosure of only these three particular fatty alcohols having this property is insufficient to enable the skilled person to carry out the invention over the whole of the broad field claimed.

Moreover, claim 1 appears to characterize a chemical composition by its parameters (a certain DSC profile). This claim is not clear as the parameter used does not appear to be usual in the art, and therefore, does not allow a meaningful comparison with the prior art.

As a consequence, the search has been limited to hair conditioning compositions comprising at least 3% of a fatty alcohol having a melting point of at least 25°C together with

1/ an emulsifying agent selected from amines, betaines and nonionic compounds

2/ a breakable visible particle comprising as structural material polysaccharides, saccharides or derivatives thereof

3/ a quaternary compound

4/ an aqueous carrier.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/00018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5726137 A	10-03-1998	US 5346642 A	13-09-1994
		US 5213716 A	25-05-1993
		US 5051250 A	24-09-1991
		AU 674255 B	12-12-1996
		AU 7757594 A	25-05-1995
		BR 9404485 A	11-07-1995
		FR 2712490 A	24-05-1995
		ZA 9408478 A	29-04-1996
		AT 118165 T	15-02-1995
		AT 125689 T	15-08-1995
		AU 640143 B	19-08-1993
		AU 5755690 A	10-10-1991
		CA 2019353 A	09-10-1991
		CN 1055482 A	23-10-1991
		DD 295309 A	31-10-1991
		DE 69016715 D	23-03-1995
		DE 69016715 T	28-09-1995
		DE 69021288 D	07-09-1995
		DK 413417 T	17-07-1995
		EP 0410567 A	30-01-1991
		EP 0407040 A	09-01-1991
		EP 0413416 A	20-02-1991
		EP 0413417 A	20-02-1991
		EP 0407042 A	09-01-1991
		EP 0559304 A	08-09-1993
		FI 903130 A	10-10-1991
		GR 90100468 A,B	30-07-1992
		HU 210756 B	28-07-1995
		JP 3291212 A	20-12-1991
		MX 173747 B	25-03-1994
		NO 178748 B	19-02-1996
		NZ 234192 A	26-08-1994
		PL 165265 B	30-12-1994
		PT 94423 A,B	31-10-1991
		TR 28235 A	09-04-1996
		US 5580494 A	03-12-1996
		US 5348736 A	20-09-1994
		AT 131034 T	15-12-1995
		AU 5755890 A	03-01-1991
		CA 2019341 A	21-12-1990
		CA 2019352 A	21-12-1990
		CA 2019358 A	21-12-1990
		CN 1048422 A	09-01-1991
		DD 295404 A	31-10-1991
		DE 69023969 D	18-01-1996
		EP 0407041 A	09-01-1991
		GR 90100471 A	15-11-1991
		JP 3051367 A	05-03-1991
		PT 94418 A	08-02-1991
EP 0795317 A	17-09-1997	DE 19610458 C	10-07-1997
		DE 19610459 C	10-07-1997
		BR 9701310 A	29-09-1998
		ES 2108668 T	01-01-1998
		JP 9249525 A	22-09-1997
		US 5885561 A	23-03-1999
US 5468496 A	21-11-1995	FR 2699404 A	24-06-1994

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: al Application No

PCT/US 99/00018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5468496 A		AT 140150 T CA 2111753 A DE 69303588 D DE 69303588 T DE 603080 T DK 603080 T EP 0603080 A ES 2056762 T GR 94300062 T GR 3021007 T JP 2512282 B JP 6211628 A	15-07-1996 19-06-1994 14-08-1996 06-02-1997 06-04-1995 25-11-1996 22-06-1994 16-10-1994 30-09-1994 31-12-1996 03-07-1996 02-08-1994
JP 60078907 A	04-05-1985	NONE	
WO 9723194 A	03-07-1997	AU 1211397 A DE 19681727 T	17-07-1997 12-05-1999
WO 9731616 A	04-09-1997	AU 1979197 A AU 4580896 A AU 7675696 A CA 2229227 A CA 2229235 A EP 0859587 A EP 0859586 A WO 9731617 A	16-09-1997 04-09-1997 16-09-1997 04-09-1997 04-09-1997 26-08-1998 26-08-1998 04-09-1997